CALCULATION OF THE HEAT CAPACITIES OF MOLECULAR LIQUIDS

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CALCULATION OF THE HEAT CAPACITIES

OF MOLECULAR LIQUIDS

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Abstract of Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering in 1951.

CALCULATION OF THE HEAT CAPACITIES OF MOLECULAR LIQUIDS

Heat capacity, compressibility, and density data have been collected for carbon tetrachloride, carbon disulfide, chloroform, methylene dichloride, ethylene dichloride, ethylene dibromide, n-heptane, acetone, benzene, toluene, m-xylene, and fluorobenzene. These data have been used to calculate the heat capacities at constant volume of the above listed liquids in the temperature range between 273.2 and 353.2 degrees Kelvin. Differences between the heat capacities at constant pressure and the heat capacities at constant volume have also been tabulated.

An extramolecular contribution* to the heat capacity of the liquid has been defined as the difference between the heat capacity at constant volume and the heat capacity arising from the internal motions of the molecule. The latter term has been calculated for each liquid from the internal vibration frequencies of the molecule or from zero pressure heat capacities of gases.

Extramolecular contributions, as defined above, have been calculated for the liquids listed above in the temperature range stated above

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*R. C. Lord, Jr., "The Heat Capacities of Molecular Lattices I. Introduction," J. Chem. Phys., 9: 693-699, 1941. Lord has used this term to describe the lattice contribution for the solid.

and correlated by plotting against a reduced temperature

$$\theta = \frac{\text{Temperature of Liquid - Temperature of Fusion}}{\text{Critical Temperature - Temperature of Fusion}}$$

defined by Bauer, Magat, and Surdin.**

It was found that liquids consisting of non-linear molecules follow a single curve.

The extramolecular contribution to heat capacity at the melting point (i.e., $\theta = 0$) was found to be approximately 12 cal/mole-^{o}K, the high temperature limit for the lattice contribution of an ideal non-linear molecular solid, and to decrease to approximately 10 cal/mole-^{o}K at $\theta = 0.45$. This correlation has been used to estimate the heat capacities of liquids at values of θ less than 0.5.

Carbon tetrachloride does not follow the same curve as the other non-linear molecular liquids examined. The cause of this departure was attributed to free rotation of carbon tetrachloride molecules in the liquid.

The extramolecular contribution to the heat capacity of carbon disulfide, which consists of linear molecules, was found to be approximately 8 cal/mole-^{o}K between $\theta = 0.25$ and $\theta = 0.4$, and evidently follows the same curve as the diatomic liquid, air, investigated by Bauer, Magat, and Surdin.***

**E. Bauer, M. Magat, and M. Surdin, "Reduced Temperature and General Properties of Pure Liquids," Trans. Faraday Soc., 33: 81-87, 1937.

***Ibid.

CALCULATION OF THE HEAT CAPACITIES OF MOLECULAR LIQUIDS

CHAPTER I

INTRODUCTION

Purpose and Scope

The purpose of this thesis is to present a method for estimating the heat capacities of liquids based on certain similarities of the liquid state with the solid state on one hand, and with the gaseous state on the other hand. The scope of this thesis is restricted primarily to the "normal", or non-associated molecular liquids.

This introduction will present brief reviews of the methods for calculating the heat capacities of ideal gases and of solids and describe the approach of this thesis to the problem for liquids.

Gases

The heat capacity at constant volume of an ideal gas may be represented as the sum of several contributions, each due to a particular kind of motion of or within the molecule, namely: translation through space, rotation about three principal axes, and several modes of motion (mainly vibration between the atoms) within the molecule.

Under ordinary conditions, the translational contribution is set equal to (3/2) R, R being the gas constant, while the rotational contribution is set equal to (2/2) R or (3/2) R depending upon whether the molecules of the gas are linear or non-linear. For monatomic gases the

translational contribution constitutes the total heat capacity at constant volume if excited electronic states are neglected. The vibrational contribution for polyatomic gases may be calculated from characteristic vibration frequencies determined by spectroscopic investigation. In some cases, one or more of the vibrational frequencies is replaced by a contribution due to internal rotation.

Solids

The heat capacity at constant volume for monatomic crystalline solids has been satisfactorily explained by the Debye theory.[1] The Debye function expresses the heat capacity in terms of harmonic vibrations in 3N degrees of freedom, N being the number of atoms in the crystal.

Andrews,[2,3] and Lord, Ahlberg, and Andrews[4] have expressed the heat capacity of a molecular solid, benzene, as the sum of a lattice and an internal contribution. The three degrees of translation and three degrees of rotation of the molecular lattice were taken to give rise to compressional and torsional waves which take up energy in the manner described by the Debye function.

If one assumes that the Debye Θ for the compressional and torsional modes of motion are the same, then the heat capacity at constant

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[1] P. Debye, "Theory of Specific Heats," Ann. Physik., 39:789-839, 1912 (Chemical Abstracts, 7: 2891, 1913).

[2] D. H. Andrews, "The Distribution of Thermal Energy in Organic Molecules," Proc. K. Akad. Amst., 29: 744-753, 1926 (Chemical Abstracts, 22: 14, 1928).

[3] D. H. Andrews, "Valence Forces as Calculated from Specific Heats and Absorption Spectra," Chem. Rev., 5: 533-547, 1928.

[4] R. C. Lord, Jr., J. E. Ahlberg, and D. H. Andrews, "Calculation of the Heat Capacity Curves of Crystalline Benzene and Benzene-d_6," J. Chem. Phys., 5: 649-654, 1937.

volume can be represented by the expression

$$C_v = 6RD(\theta/T) + \sum_{i=1}^{i=n} RE(h\nu_i/kT).$$

In this expression $D(\theta/T)$ is the Debye heat capacity function and $E(h\nu_i/kT)$ is the Einstein heat capacity function, respectively, for one degree of freedom. The sum of the latter extends over all the internal frequencies, n, of the molecule. For purposes of this calculation the frequencies determined for the molecule in the gaseous state are usually used.

Lord[5] has discussed this type of calculation in considerable detail. Brucksch and Ziegler[6] have used this method of representing C_v for a number of other molecular solids. For linear molecules the lattice contribution of the above expression should be changed to $5RD(\theta/T)$. At elevated temperatures, the Debye function approaches the value unity; hence, the lattice contribution to the heat capacity, C_v, may approach 6R for molecular solids consisting of non-linear molecules and 5R for those consisting of linear molecules. Because of the low value of the Debye θ characteristic of most molecular solids, this limit is usually attained somewhat below the melting point.

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[5] R. C. Lord, Jr., "The Heat Capacities of Molecular Lattices; I. Introduction," J. Chem. Phys., 9:693-699, 1941. Lord has used this word to describe the lattice contribution for a solid.

[6] W. F. Brucksch, Jr., and W. T. Ziegler, "The Heat Capacities of Molecular Lattices; III. Some Simple Molecular Solids," J. Chem. Phys., 10: 740-743, 1942.

Liquids

The approach adopted in the present attempt to understand the heat capacity of molecular liquids was to consider the heat capacity at constant volume to consist of two parts, as has been done for solids and gases, namely: (1) an internal contribution due to the absorption of energy by the atomic vibrations within the molecule, and (2) an external, or extramolecular,[5] contribution due to the motion of the molecule as a whole.

The idea of partitioning the heat capacity of molecular liquids in the above manner is not, however, new. Paramasivan[7] has proposed just such a division for the heat capacity at constant volume of molecular liquids, his extramolecular portion being represented by a Debye function for which the mean characteristic temperature was evaluated by the formula of Lindemann.[8] Ziegler has subtracted the heat capacity of liquid benzene from that of liquid benzene-d_6 and used the difference to show that two previously assigned frequencies for benzene-d_6 were too low.[9] This involved the assumption that extramolecular contributions to heat capacity are very nearly equal for benzene and benzene-d_6 liquids, as well as the assumption that respective differences

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[7] S. Paramasivan, "Specific Heat in Relation to Raman Effect Data," Indian Journal of Physics, 6: 413-420, 1931.

[8] F. A. Lindemann, "Calculation of Molecular Vibration Frequencies," Physikal Z., 11:609-612, 1910 (Chemical Abstracts, 4: 2593, 1910).

[9] W. T. Ziegler, "Heat Capacity Studies at Low Temperatures," unpublished doctoral dissertation (Baltimore: Johns Hopkins University, 1938), p. 20.

between heat capacities at constant pressure and heat capacities at constant volume are equal for these two liquids.

The procedure adopted in the present work was to calculate the internal contributions for a number of molecular liquids throughout a considerable temperature range and to subtract these values from the corresponding heat capacities at constant volume in order to obtain extramolecular contributions to heat capacity, which were then compared, and also examined in the light of the corresponding theoretical quantities for solids and gases.

It was expected that at temperatures near the melting point these extramolecular contributions would approximate the high temperature Debye limit for ideal molecular solids, that is, 6R (roughly 12 cal/mole-deg) for non-linear molecular solids, and 5R (roughly 10 cal/mole-deg) for linear molecular solids. The reasons for this expectation were certain known similarities in the properties of liquids and solids near the melting point, leading to the conclusion that the molecular organization in a liquid at these temperatures is similar to that in the solid and that the heat motion is oscillatory in character. The evidence supporting this point of view has been aptly summarized by Frenkel.[10] The fact that the heat capacities of solids and of the corresponding liquids are not very different in value near the melting point is sufficient for the present work.

It would seem reasonable, however, that the oscillatory character of the heat motion of liquids would not continue as the temperature of

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[10] J. Frenkel, Kinetic Theory of Liquids (New York: Oxford University Press, 1946), p. 93.

the liquid is raised, but that with expansion of the lattice, the oscillations must give way to restricted rotation and translation. At sufficiently high temperatures, the rotation and translation may approach the free condition as in the gas. In any case, the heat capacity at constant volume of liquids at high temperatures approaches that of the corresponding gases.[11]

Bhagavantam[12] has discussed the specific heats of liquids from this viewpoint and calculated the specific heats of liquid benzene, carbon tetrachloride, and carbon disulfide on the assumption that the extramolecular contribution for the liquid is (1) the same as for the solid, and (2) the same as for the gas. He compared his results with experimental heat capacities and found, as might be expected, that the experimental values lay between the two calculated values. For benzene, in particular, he found that the results calculated on the assumption that the extramolecular contribution was the same as for the solid agreed very well with the experimental liquid heat capacity measurements over a considerable temperature range.

Bauer, Magat, and Surdin have shown that the heat capacities at constant volume for some monatomic liquids when plotted against a reduced temperature, defined by Bauer, Magat, and Surdin, follow a single curve.[13]

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[11] J. Frenkel, "On the Liquid State and the Theory of Fusion," Trans. Faraday Soc., 33: 58-65, 1937.

[12] S. Bhagavantam, "Specific Heats of Liquids in Relation to Raman Effect Data," Proc. Indian Acad. Sci., 7A: 245-250, 1938.

[13] E. Bauer, M. Magat, and M. Surdin, "Reduced Temperature and General Properties of Pure Liquids," Trans. Faraday Soc., 33: 81-87, 1937.

They have also plotted the heat capacity at constant volume for bromine and liquid air, and found that these two diatomic liquids, also, appear to follow a single curve. The reduced temperature of Bauer, Magat, and Surdin is adopted in this thesis as the correlating tool for the extramolecular contributions of polyatomic liquids and will be defined and discussed in Chapter IV.

Method and Arrangement

The work that follows is concerned with determining the extramolecular contributions, as described previously, throughout as large a temperature range as possible for a number of molecular liquids, and with plotting these extramolecular contributions against the reduced temperature of Bauer, Magat, and Surdin. It is believed that the resulting plot may then be used (1) as a convenient aid in estimating rather closely the heat capacities for certain liquids, or (2) as an aid in discussing the probable modes of molecular motion within certain liquids.

The calculations are presented in the following order: Chapter II, the calculations of heat capacities at constant volume from heat capacities at constant pressure using standard thermodynamic relations; Chapter III, the calculations of extramolecular contributions from heat capacities at constant volume and internal contributions; and Chapter IV, the correlation of extramolecular contributions by plotting them against the reduced temperature of Bauer, Magat, and Surdin. Chapter IV also includes the discussion of results and proposed use for the correlation.

Sources of data and detailed calculations are relegated to the appendices as follows: Appendix I, sources of data and discussions of reliability for heat capacities (at constant pressure) of the liquids; Appendix II, compressibilities and density data used in the calculations for heat capacities at constant volume; Appendix III, the heat capacities of gases and calculations of internal contributions.

In connection with the present work a literature search was made for papers concerned with the theory of liquids. Papers not used for reference in the text are listed in the Bibliography under the subtitle: Papers Concerning Theory, not Specifically Referred to in the Text.

CHAPTER II

CALCULATION OF THE HEAT CAPACITY AT CONSTANT VOLUME

Method of Calculation

The heat capacity at constant volume, C_v, for the liquid, may be calculated using the exact thermodynamic relation

$$C_p/C_v = K_T/K_S \tag{1}$$

where C_p is the heat capacity at constant pressure, and K_T and K_S are the isothermal and adiabatic compressibilities, respectively.

C_v may also be calculated from the thermodynamic relation

$$C_p - C_v = TV(a)^2/K_T \tag{2}$$

where T is the absolute temperature, V is the molal volume, and "a" is the coefficient of thermal expansion at constant pressure.

The isothermal compressibility, adiabatic compressibility, and coefficient of thermal expansion are defined as follows:

$$K_T = -(1/V)(dV/dP)_T \tag{3}$$

$$K_S = -(1/V)(dV/dP)_S \tag{4}$$

$$a = (1/V)(dV/dT)_p \tag{5}$$

where p is the absolute pressure and S is the entropy.

The coefficient of thermal expansion, a, is readily obtained by differentiation of an equation describing variation of density with temperature for the liquid under consideration.

A survey of the literature revealed that the adiabatic compressibilities are more generally available than isothermal compressibilities. This arises from the fact that the adiabatic compressibility can be readily calculated from the velocity of sound in liquids through the relation

$$K_S = V(v_s)^2 \tag{6}$$

where v_s is the velocity of sound.

The procedure generally used in this thesis was to calculate C_v from Equation (1), using the experimental values for C_p and K_S, and the value of K_T obtained from the relation

$$K_T = K_S + TV(a)^2C_p, \tag{7}$$

an expression readily derived by combining Equations (1) and (2). The results of these calculations are shown in Table I.

It has not been necessary in all cases, however, to make the calculation for isothermal compressibility, since some investigators reporting adiabatic compressibilities have done this already and reported their results. The reliability of these results will be discussed in Appendix II.

a. Sample Calculation for Heat Capacity at Constant Volume

Liquid: Carbon Tetrachloride

$T = 273.2^{\circ}K$
$C_p = 31.26$ cal/mole-$^{\circ}K$
$K_S = 62 \times 10^{-6}$ atm^{-1}
$1/V = 1.6326$ g/cc
$a = 1.171 \times 10^{-3}$ $^{\circ}K^{-1}$

Molecular Weight = 153.84
1 cc-atm = 0.024218 cal.

$$K_T \times 10^6 = K_S \times 10^6 + T(a \times 10^3)^2(153.84)(0.02422)/(\tfrac{1}{V})C_p$$

$$= 62 + 273.2(1.171)^2(153.84)(0.02422)/(1.6326)31.26$$

$$= 62 + 27.3$$

$$= 89.3 \text{ atm}^{-1}$$

$$C_v = \frac{K_S \times 10^6}{K_T \times 10^6} C_p$$

$$= \frac{62}{89.3} (31.26)$$

$$= 21.70 \text{ cal/mole-}^\circ\text{K}$$

Reliability of Results

The reliability of the results for the calculations of C_v depends upon the accuracy of the C_p, K_S, and density data used. These data are discussed in detail in Appendices I and II.

The C_p values used were, in general, taken from "best curves" drawn through all the data found for each liquid. For methylene dichloride, however, only one source for C_p was found.

For all the liquids, the values used are within one per cent of all the data; consequently, the accuracy of the calculated C_v, in so far as they depend on C_p, is believed to be within one per cent.

The agreement between the several sources of adiabatic compressibilities is very good. The small differences that occur between various K_S data would affect the C_v results practically not at all, provided the values of K_T calculated from them through the use of Equation (7) introduce no significant errors.

For six of the liquids of Table I, calculations of K_T were not made in this thesis (as indicated in the table). K_T results were used which were taken from the same sources as the K_S data. On the basis

TABLE I

RESULTS OF CALCULATIONS FOR HEAT CAPACITIES AT CONSTANT VOLUME*

Liquid	T °K	C_p cal/mole-°K	$K_S \times 10^6$ atm^{-1}	1/V g/cc	$a \times 10^3$ $°K^{-1}$	$K_T \times 10^6$ atm^{-1}	C_v cal/mole-°K
Carbon Tetrachloride	263.2	31.06	57.0	1.6516	1.14871	82.2	21.54
	273.2	31.26	62.0	1.6326	1.17056	89.3	21.70
	283.2	31.38	67.0	1.6134	1.19293	96.6	21.76
	293.2	31.48	72.6	1.5941	1.21614	104.8	21.81
	303.2	31.58	78.4	1.5746	1.23993	113.3	21.85
	313.2	31.64	84.8	1.5550	1.26443	122.7	21.87
	323.2	31.72	92.0	1.5353	1.28967	133.1	21.93
	333.2	31.80	98.4	1.5154	1.31569	143.0	21.88
Carbon Disulfide	273.2	18.01	53.21			81.44	11.76
	283.2	18.08	56.79	(The calculation		87.52	11.73
	293.2	18.18	60.50	for K_T not made		93.84	11.72
	303.2	18.41	64.52	in this thesis.)		100.55	11.74
	313.2	18.41	69.08			107.92	11.78
Chloroform	273.2	27.35	58.54			85.90	18.63
	283.2	27.56	62.98			92.94	18.68
	293.2	27.80	68.31	(The calculation		101.15	18.77
	303.2	28.06	74.10	for K_T not made		110.04	18.89
	313.2	28.32	80.48	in this thesis.)		119.96	19.00
	323.2	28.58	87.33			130.74	19.09
	333.2	28.82	94.70			142.46	19.16

(continued on next page)

TABLE I
(continued)

Liquid	T °K	C_p cal/mole-°K	$K_S \times 10^6$ atm^{-1}	1/V g/cc	$a \times 10^3$ $°K^{-1}$	$K_T \times 10^6$ atm^{-1}	C_v cal/mole-°K
Methylene Dichloride	253.2	23.34	46.37	1.3986	1.2633	71.83	15.06
	273.2	23.44	54.15	1.3624	1.3208	84.85	14.96
	283.2	23.57	58.83	1.3441	1.3590	92.99	14.92
	293.2	23.75	63.95	1.3263	1.3936	101.16	15.02
	303.2	23.98	69.77	1.3073	1.4348	110.73	15.11
	313.2	24.26	76.32	1.2887	1.4765	121.51	15.24
Ethylene Dichloride	253.2	30.25	38.23			55.30	20.91
	273.2	30.52	48.0			69.0	21.23
	283.2	30.65	51.0	(The calculation		74.0	21.12
	293.2	30.79	55.0	for K_T not made		80.0	21.16
	303.2	30.94	59.0	in this thesis.)		86.0	21.23
	313.2	31.15	64.0			92.5	21.55
	323.2	31.40	69.0			100.0	21.67
Ethylene Dibromide	283.2	32.35	42.87	2.2014	0.9514	60.09	23.08
	293.2	32.45	45.70	2.1804	0.9624	63.85	23.23
	303.2	32.55	48.59	2.1594	0.9736	67.70	23.36
	313.2	32.65	51.75	2.1384	0.9850	72.33	23.36
	323.2	32.75	55.16	2.1173	0.9967	76.30	23.68
Fluorobenzene**	293.2	34.94	69.93	1.0229	1.166	95.86	25.49
	303.2	35.12	76.03	1.0108	1.201	104.7	25.50
	313.2	35.45	82.47	0.9987	1.241	114.1	25.61
	323.2	36.10	90.35	0.9864	1.285	125.2	26.04

(continued on next page)

TABLE I
(continued)

Liquid	T °K	C_p cal/mole-°K	$K_S \times 10^6$ atm^{-1}	1/V g/cc	$a \times 10^3$ $°K^{-1}$	$K_T \times 10^6$ atm^{-1}	C_v cal/mole-°K
Acetone	273.2	29.13	77.0	0.81248	1.3538	106.8	21.00
	283.2	29.50	83.5	0.80139	1.3940	116.2	21.20
	293.2	29.90	90.6	0.79014	1.4356	126.6	21.40
	303.2	30.32	99.1	0.77871	1.4785	138.6	21.68
	313.2	30.77	108.8	0.76711	1.5234	153.9	21.75
	323.2	31.21	120.1	0.75534	1.5698	169.6	22.10
n -Heptane	183.2	48.04	34.28	0.7738	1.0145	46.59	35.35
	203.2	48.18	44.37	0.7580	1.0521	59.31	36.04
	223.2	48.67	56.94	0.7420	1.0916	74.81	37.04
	243.2	49.55	70.46	0.7256	1.1335	91.55	38.14
	263.2	50.90	85.79	0.7092	1.1774	110.31	39.59
	283.2	52.44	102.4	0.6927	1.2206	130.58	41.12
	303.2	54.18	121.4	0.6755	1.2588	153.25	42.92
	323.2	56.10	145.8	0.6577	1.3197	182.82	44.74
	343.2	58.20	170.1	0.6395	1.4045	214.24	46.21
	363.2	60.34	198.4	0.6210	1.5150	252.38	47.43
Benzene	283.2	31.56	60.8	(The calculation for K_T not made in this thesis.)		88.1	21.78
	293.2	32.08	65.9			95.7	22.09
	303.2	32.67	72.0			103.3	22.77
	313.2	33.30	78.0			111.5	23.29
	323.2	33.94	85.1			120.6	23.95
	333.2	34.58	93.2			130.0	24.72
	343.2	35.18	102.3			143.0	25.17
	353.2	35.72	111.5			156.0	25.53

(continued on next page)

TABLE I
(continued)

Liquid	T °K	C_p cal/mole-°K	$K_S \times 10^6$ atm^{-1}	1/V g/cc	$a \times 10^3$ $°K^{-1}$	$K_T \times 10^6$ atm^{-1}	C_v cal/mole-°K
Toluene	283.2	36.73	62.8	(The calculation for K_T not made in this thesis.)		85.1	27.11
	293.2	37.23	67.9			91.2	27.72
	303.2	37.86	72.5			97.3	28.20
	313.2	38.58	78.0			104.4	28.84
	323.2	39.39	84.1			112.5	29.45
	333.2	40.23	91.2			121.6	30.17
	343.2	41.09	98.3			131.2	30.78
m-Xylene	273.2	41.37	57.76	(The calculation for K_T not made in this thesis.)		74.99	31.86
	283.2	42.48	61.81			80.56	32.59
	293.2	43.58	65.86			86.13	33.29
	303.2	44.69	69.92			91.20	34.26
	313.2	45.79	75.49			97.28	35.53
	323.2	46.90	81.06			104.4	36.43
	333.2	48.01	87.14			111.5	37.53
	343.2	49.11	93.22			119.6	38.29
	353.2	50.21	100.32			127.7	39.45

*
a - Coefficient of Thermal Expansion: reciprocal degrees Kelvin.
C_p - Heat Capacity at Constant Pressure: calories/mole-degrees Kelvin.
C_v - Heat Capacity at Constant Volume: calories/mole-degrees Kelvin.
K_S - Adiabatic Compressibility: reciprocal atmospheres.
K_T - Isothermal Compressibility: reciprocal atmospheres.
T - Absolute Temperature: degrees Kelvin.
1/V - Density: grams/cubic centimeter.

**The author is indebted to Mr. R. C. Adams for collecting the data and making the calculations for fluorobenzene.

of the discussion of isothermal compressibilities in Appendix II, it is believed that these K_T introduced no error in calculated C_v greater than one per cent. For the remaining six liquids of Table I, K_T values were calculated in this thesis. The error introduced by the use of these K_T is less than one per cent.

It is estimated, on the basis of the preceeding discussion, that the calculated C_v of Table I are all within two per cent of probable true values, excepting the three lower temperature extrapolations for n-heptane (discussed in Appendix II).

CHAPTER III

CALCULATION OF THE EXTRAMOLECULAR CONTRIBUTION TO HEAT CAPACITY

Definition and Method of Calculation

The extramolecular contribution to the heat capacity, C_v, of a liquid is defined as $C_v - C_i$, the difference between the heat capacity at constant volume and the internal contribution to the heat capacity. This quantity for a liquid, therefore, corresponds to the lattice contribution for a solid, or to the sum of the translational and rotational contributions for a gas, as stated in Chapter I.

Results of the calculations for C_v were given in Chapter II.

Since spectroscopic investigations of liquids and of gases have indicated that for substances which are not highly associated in the liquid state the differences between the internal vibration frequencies for the molecule in these phases, respectively, are small,[14] it was assumed that the internal contribution for such a substance at a single temperature is the same whether the substance be in the liquid or the gaseous state. The internal contributions, C_i, for the liquids of this thesis were, therefore, either calculated from internal vibration frequencies, without regard to whether these frequencies had been determined from investigations of liquids or of gases; or, obtained from calculated gas heat capacities, C_p^0, found in the literature. In this connection, it was noted that frequencies determined for the

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[14] G. Herzberg, Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules (New York: D. Van Nostrand Co., Inc., 1945), pp. 534-537.

molecule in the liquid have often been used in calculations of gas heat capacities.[15]

C_i may also be obtained from experimental C_p^0 data when these data are known for temperatures where the liquid exists, but such data are rare.

C_i is obtained from C_p^0 by subtracting 4R, R being the gas constant, if the molecule is non-linear; or, by subtracting (7/2)R if the molecule is linear.

The results of the calculations of $C_v - C_i$ are given in Table II, and detailed calculations of C_i, together with discussions of the data used, in Appendix III.

Bhagavantam[16] has made similar calculations for benzene, carbon tetrachloride, and carbon disulfide. The results in this thesis for these liquids, in general, confirm the results of Bhagavantam. The results of his calculations are shown in Table II, with the corresponding results of the present work.

Reliability of Results

The accuracy of the extramolecular contributions to heat capacity calculated in this chapter depends upon the accuracy of the heat capacities at constant volume calculated in Chapter II and upon the accuracy of the internal contributions to heat capacity calculated in Appendix III. The heat capacities at constant volume are believed to be accurate within two per cent of the results reported.

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[15] R. D. Vold, "The Heat Capacity of Methane and Its Halogen Derivatives from Spectroscopic Data," J. Am. Chem. Soc., 57:1192-1195,1935.

[16] S. Bhagavantam, loc. cit.

TABLE II

RESULTS OF CALCULATIONS FOR EXTRAMOLECULAR CONTRIBUTIONS*

Liquid	T °K	C_p cal/mole-°K	$C_p - C_v$ cal/mole-°K	C_v cal/mole-°K	C_i cal/mole-°K	$C_v - C_i$ cal/mole-°K	
						This Thesis	Bhagavantam
Carbon Tetrachloride	273.2	31.26	9.56	21.70	11.35	10.35	9.71
	283.2	31.38	9.62	21.76	11.63	10.13	
	293.2	31.48	9.67	21.81	11.89	9.92	9.45
	303.2	31.58	9.73	21.85	12.14	9.71	
	313.2	31.64	9.77	21.87	12.38	9.49	9.17
	323.2	31.72	9.79	21.93	12.60	9.33	
	333.2	31.80	9.92	21.88	12.82	9.06	9.47
Carbon Disulfide	273.2	18.01	6.25	11.76	3.64	8.12	8.06
	283.2	18.08	6.35	11.73	3.76	7.97	
	293.2	18.18	6.46	11.72	3.88	7.84	7.81
	303.2	18.30	6.56	11.74	4.00	7.74	
	313.2	18.41	6.63	11.78	4.11	7.67	7.65
Chloroform	273.2	27.35	8.72	18.63	7.16	11.47	
	283.2	27.56	8.88	18.68	7.42	11.26	
	293.2	27.80	9.03	18.77	7.67	11.10	
	303.2	28.06	9.17	18.89	7.91	10.98	
	313.2	28.32	9.32	19.00	8.14	10.86	
	323.2	28.58	9.49	19.09	8.37	10.72	
	333.2	28.82	9.66	19.16	8.59	10.57	
Methylene Dichloride	253.2	23.34	8.28	15.06	3.33	11.73	
	273.2	23.44	8.48	14.96	3.76	11.20	
	283.2	23.57	8.65	14.92	3.98	10.94	
	293.2	23.75	8.73	15.02	4.20	10.82	
	303.2	23.98	8.87	15.11	4.42	10.69	
	313.2	24.26	9.02	15.24	4.63	10.61	

(continued on next page)

TABLE II
(continued)

Liquid	T °K	C_p cal/mole-°K	$C_p - C_v$ cal/mole-°K	C_v cal/mole-°K	C_i cal/mole-°K	$C_v - C_i$ cal/mole-°K	
						This Thesis	Bhagavantam
Ethylene Dichloride	253.2	30.25	9.34	20.91	9.30	11.61	
	273.2	30.52	9.29	21.23	9.90	11.33	
	283.2	30.65	9.53	21.12	10.10	11.02	
	293.2	30.79	9.63	21.16	10.40	10.76	
	303.2	30.94	9.71	21.23	10.80	10.43	
	313.2	31.15	9.60	21.55	11.10	10.45	
	323.2	31.40	9.73	21.67	11.40	10.27	
Ethylene Dibromide	283.2	32.35	9.27	23.08	11.37	11.71	
	293.2	32.45	9.22	23.23	11.73	11.50	
	303.2	32.55	9.19	23.36	12.13	11.23	
	313.2	32.65	9.29	23.36	12.53	10.83	
	323.2	32.75	9.07	23.68	12.92	10.76	
Fluorobenzene**	293.2	34.94	9.45	25.49	15.05	10.44	
	303.2	35.12	9.62	25.50	15.70	9.80	
	313.2	35.45	9.84	25.61	16.35	9.26	
	323.2	36.10	10.06	26.04	17.00	9.04	
Acetone	273.2	29.13	8.13	21.00	9.39	11.61	
	283.2	29.50	8.30	21.20	9.70	11.50	
	293.2	29.90	8.50	21.40	10.05	11.35	
	303.2	30.32	8.64	21.68	10.50	11.18	
	313.2	30.77	9.02	21.75	10.90	10.85	
	323.2	31.21	9.11	22.10	11.50	10.60	

(continued on next page)

TABLE II
(continued)

Liquid	T °K	C_p cal/mole-°K	$C_p - C_v$ cal/mole-°K	C_v cal/mole-°K	C_i cal/mole-°K	$C_v - C_i$ cal/mole-°K	
						This Thesis	Bhagavantam
n-Heptane	183.2	48.04	12.69	35.35	21.91	13.44	
	203.2	48.18	12.14	36.04	23.46	12.58	
	223.2	48.67	11.63	37.04	25.08	11.96	
	243.2	49.55	11.41	38.14	26.90	11.24	
	263.2	50.90	11.31	39.59	28.59	11.00	
	283.2	52.44	11.32	41.12	30.66	10.46	
	303.2	54.18	11.26	42.92	32.62	10.30	
	323.2	56.10	11.36	44.74	34.68	10.06	
	343.2	58.20	11.99	46.21	36.85	9.36	
	363.2	60.34	12.91	47.43	38.88	8.55	
Benzene	283.2	31.56	9.78	21.78	10.34	11.44	
	293.2	32.08	9.99	22.09	11.01	11.08	11.08
	303.2	32.67	9.90	22.77	11.72	11.05	
	313.2	33.30	10.01	23.29	12.44	10.85	10.56
	323.2	33.94	9.99	23.95	13.13	10.82	
	333.2	34.58	9.86	24.72	13.83	10.89	10.23
	343.2	35.18	10.01	25.17	14.52	10.65	
	353.2	35.72	10.19	25.53	15.22	10.31	
Toluene	283.2	36.73	9.62	27.11	15.45	11.66	
	293.2	37.23	9.51	27.72	16.36	11.36	
	303.2	37.86	9.66	28.20	17.27	10.93	
	313.2	38.58	9.74	28.84	18.15	10.69	
	323.2	39.39	9.94	29.45	19.04	10.41	
	333.2	40.23	10.06	30.17	19.85	10.32	
	343.2	41.09	10.31	30.78	20.67	10.11	

(continued on next page)

TABLE II
(continued)

Liquid	T °K	C_p cal/mole-°K	$C_p - C_v$ cal/mole-°K	C_v cal/mole-°K	C_i cal/mole-°K	$C_v - C_i$ cal/mole-°K	
						This Thesis	Bhagavantam
	273.2	41.37	9.51	31.86	20.25	11.61	
	283.2	42.48	9.89	32.59	21.25	11.34	
	293.2	43.58	10.29	33.29	22.05	11.24	
	303.2	44.69	10.43	34.26	23.07	11.19	
m-Xylene	313.2	45.79	10.26	35.53	24.08	11.45	
	323.2	46.90	10.47	36.43	25.06	11.37	
	333.2	48.01	10.48	37.53	26.04	11.49	
	343.2	49.11	10.82	38.29	26.95	11.34	
	353.2	50.21	10.76	39.45	27.87	11.58	

*
T - Absolute Temperature: degrees Kelvin.
C_p - Heat Capacity at Constant Pressure: calories/mole-degrees Kelvin.
C_v - Heat Capacity at Constant Volume: calories/mole-degrees Kelvin.
C_i - Internal Contribution to Heat Capacity: calories/mole-degrees Kelvin.

**The author is indebted to Mr. R. C. Adams for making the calculations concerning fluorobenzene.

It is well known that C_p^o calculated for gases from vibration frequencies are more accurate than the corresponding results of direct measurements of gas heat capacities, provided the frequencies are correctly assigned. The former procedure generally gives results within 0.25 cal/mole-°K of probable true values. Wherever possible, however, gas heat capacities calculated from the internal contributions which were calculated from vibration frequencies in Appendix III have been compared with experimental measurements. When the latter were not available, calculated entropies were compared with experimental entropies to assure that the frequency assignments used are correct.

For n-heptane, ethylene dichloride, and ethylene dibromide, contributions to heat capacity due to internal rotation which have been determined by Pitzer[17] and Gwinn and Pitzer[18] from measured gas heat capacities were used in the calculations. For acetone, this contribution was determined from the potential barrier to internal rotation assigned by Schumann and Aston[19] who made the assignment by comparing the calculated with the experimental entropy.

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[17] K. S. Pitzer, "The Thermodynamics of n-Heptane and 2,2,4-Trimethylpentane, Including Heat Capacities, Heats of Fusion and Vaporization and Entropies," J. Am. Chem. Soc., 62: 1224-1227, 1940.

[18] W. D. Gwinn and K. S. Pitzer, "Gas Heat Capacity and Internal Rotation in 1,2-Dichloroethane and 1,2-Dibromoethane," J. Chem. Phys., 16: 303-309, 1948.

[19] S. C. Schumann and J. G. Aston, "The Entropy of Acetone and Isopropyl Alcohol from Molecular Data. The Equilibrium in the Dehydrogenation of Isopropyl Alcohol," J. Chem. Phys., 6: 485-488, 1938.

CHAPTER IV

CORRELATION OF THE EXTRAMOLECULAR CONTRIBUTION TO HEAT CAPACITIES OF POLYATOMIC LIQUIDS

In order to fulfill the purpose stated in Chapter I of providing a method for estimating the heat capacities of liquids, the extramolecular contributions to the heat capacities of molecular liquids calculated in Chapter III are correlated in this chapter and compared with C_v of monatomic liquids. This is preceeded by a brief discussion of the behavior of C_v for monatomic liquids.

Monatomic Liquids

The heat capacity at constant volume of a monatomic liquid may be considered to consist entirely of the translational motion (neglecting any electronic contribution) of the molecules; consequently, in the terminology of this thesis, the extramolecular contribution and C_v for monatomic liquids are identical. If the monatomic liquid is considered to be a simple Debye solid having a small characteristic temperature, θ_d, then it might be expected that C_v for such a liquid might be as large as 3R calories at the melting point and decrease with increasing temperature as the freedom of motion of the molecules become greater.

This expected behavior has been confirmed in a general way by the correlation of Bauer, Magat, and Surdin.[20] These investigators correlated the heat capacity at constant volume, C_v, by plotting C_v

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[20] E. Bauer, M. Magat, and M. Surdin, loc. cit.

against a reduced temperature[21] defined as follows:

$$\theta = (T - T_f)/(T_c - T_f) = (T/T_c - T_f/T_c)/(1 - T_f/T_c) ,$$

where T_f is the normal melting point and T_c, the critical temperature. Figure 1 is a reproduction of the plot given by Bauer, Magat, and Surdin of C_v *vs.* θ for the monatomic liquids neon, argon, and mercury and the diatomic liquids bromine and air.

It will be noted that the points representing the monatomic liquids were found to follow a single curve. Referring to Figure 1, C_v near the melting point is seen to be about 5.5 at $\theta = 0.1$, remains approximately constant to about $\theta = 0.35$, and thereafter decreases again and appears to approach 4 cal/mole-°K at the critical point.

The use of the reduced temperature scale defined above has the effect of expanding considerably the abscissa over that which would result if the more usual form of the reduced temperature (i.e., T/T_c) were used, since $\theta = 0$ when $T = T_f$ and $\theta = 1$ when $T = T_c$. It should be noted, however, that the fusion temperature, T_f, used in the function is not itself a simple function of the reduced temperature, T_f/T_c, and hence the correlating function does not correspond to the usual theorem of corresponding states.

Diatomic Liquids

Examination of the curve of C_v *vs.* θ obtained by Bauer, Magat, and Surdin for liquid bromine and air reveals that the curve is

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[21] Not to be confused with the Debye θ_d.

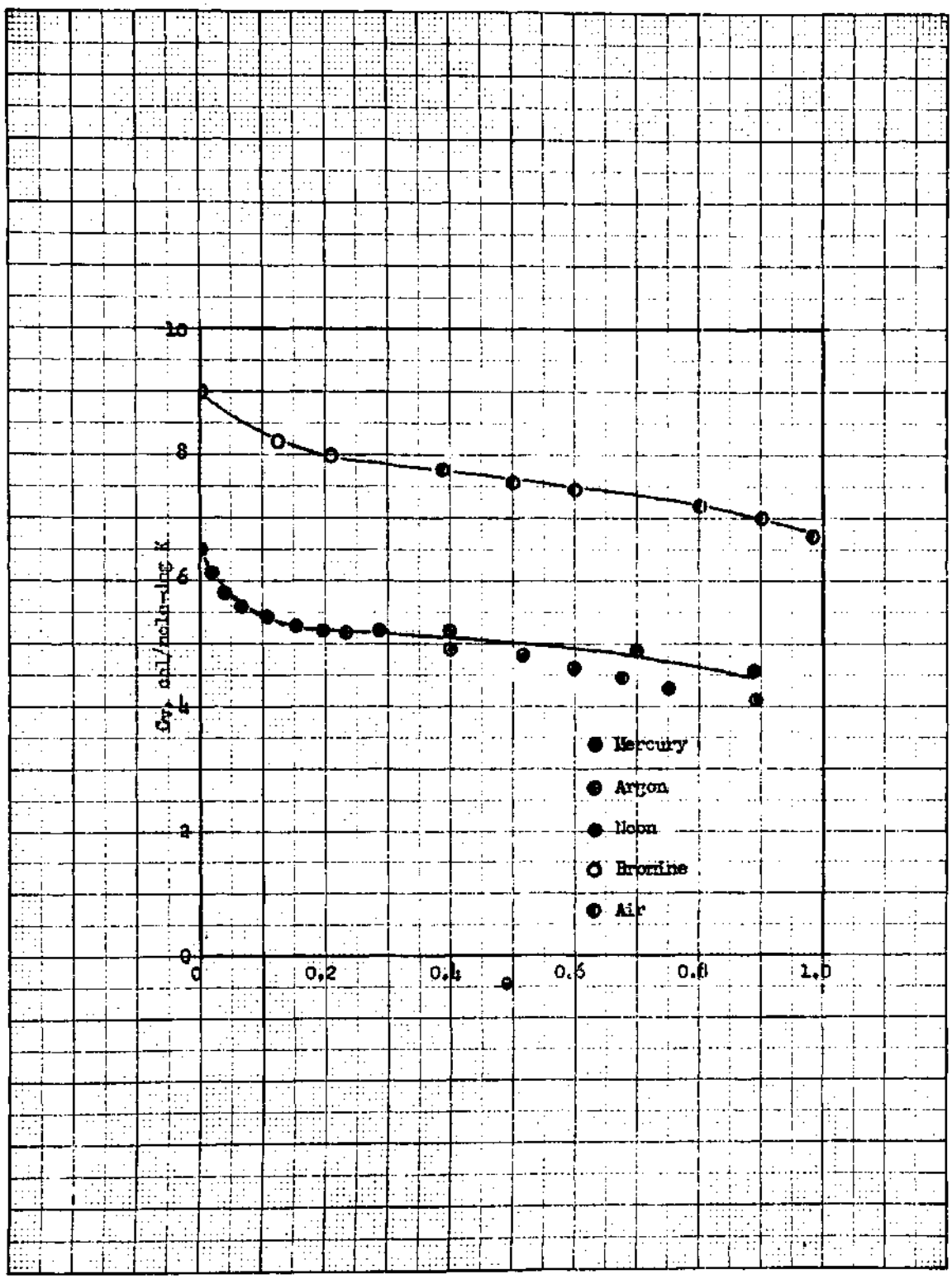

Figure 1. Plot of Bauer, Magat, and Surdin. C_v for Monatomic and Diatomic Liquids *vs.* Reduced Temperatures

parallel with but approximately 2.5 calories higher than the curve for the monatomic liquids. From the point of view of this thesis, the extramolecular heat capacity of a diatomic liquid consists of the translational and rotational portion of C_v only, that is, $C_v - C_i$, where C_i is the contribution to C_v arising from the internal frequencies of the molecule. For liquid air, which consists primarily of O_2 and N_2 molecules, the frequencies are so large and the temperature so low that C_i is zero. On the other hand, the value of C_i for bromine is not equal to zero in the temperature range for which the data are given in Figure 1; thus, when $\theta = 0$ (i.e., melting point of bromine is 265.9°K), C_i is 1.55 cal/mole-°K and increases to 1.69 cal/mole-°K at $\theta = 0.21$. The plot of C_v vs. θ for bromine is not, therefore, a plot of the extramolecular contribution to the heat capacity of the liquid in the sense of this thesis. The problem of the diatomic liquids will be discussed further when the linear molecule CS_2 is discussed.

Polyatomic Liquids

The correlation of the extramolecular contribution for polyatomic liquids has been carried out by plotting this contribution to C_v against the reduced temperature function of Bauer, Magat, and Surdin. The results thus obtained are shown in Figure 2.

Because of the difficulty mentioned above concerning the reduced temperature, θ, of Bauer, Magat, and Surdin: namely, that since T_f is not a simple function of the reduced temperature, T_f/T_c, θ does not correspond to the usual theorem of corresponding states, the extra-

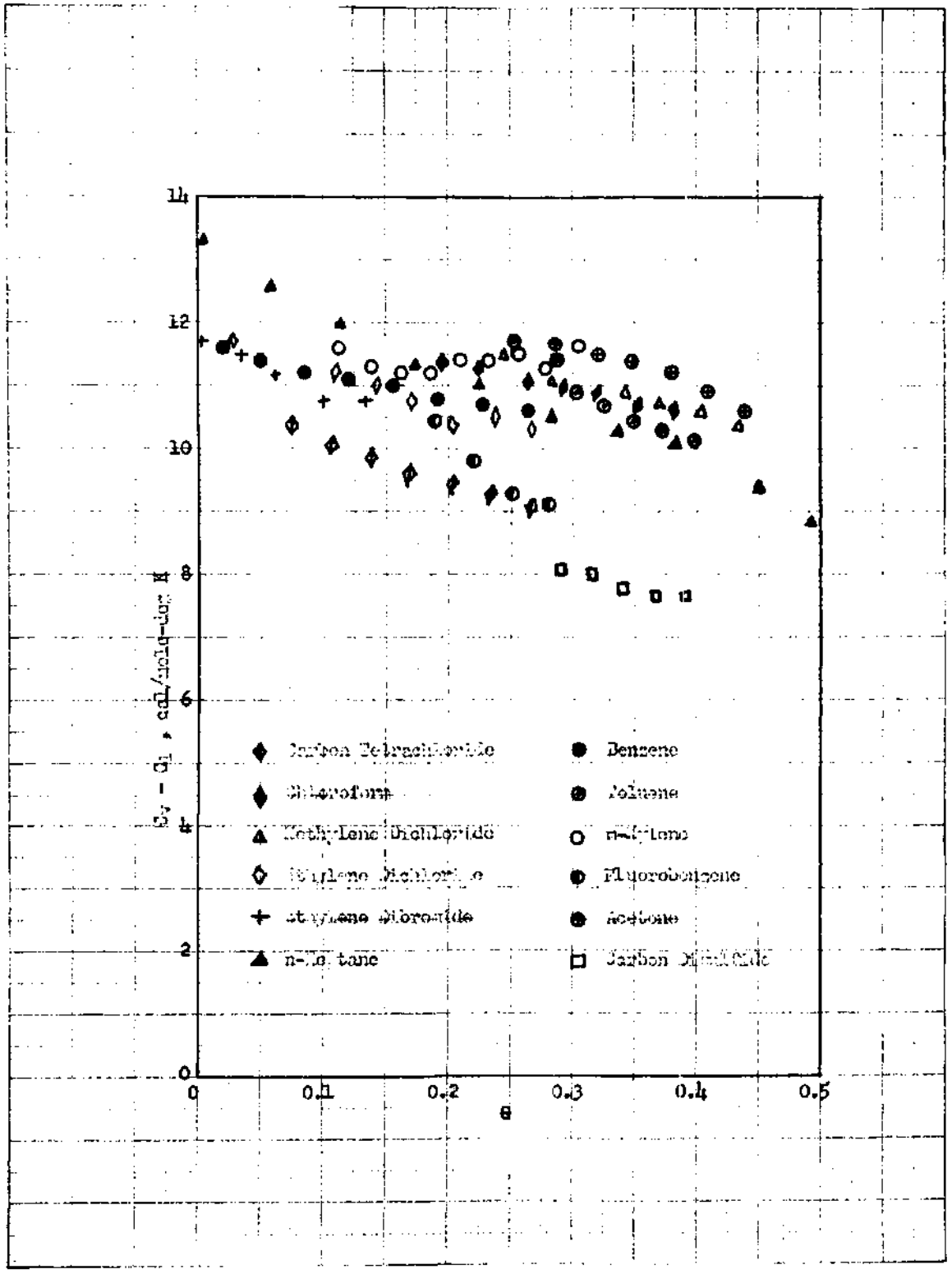

Figure 2. Plot of Extramolecular Contributions vs. Reduced Temperatures

molecular contributions were also correlated by plotting them *vs.* a reduced temperature, θ', modified so as to remove this difficulty. This modified reduced temperature was defined as

$$\theta' = (T/T_c - T_f \text{ standard}/T_c \text{ standard})/(1 - T_f \text{ standard}/T_c \text{ standard}),$$

toluene being used as the standard substance because of its low melting point. It was believed that this procedure would result in a correlation agreeing with the usual theorem of corresponding states because all liquids plotted against the abscissa expanded in this manner would be referred to the same point at low temperatures. The correlation was also made by plotting $C_v - C_i$ *vs.* the reduced temperature T/T_c directly. These correlations gave results not significantly different from the correlation using the θ of Bauer, Magat, and Surdin. The results of neither of these two additional correlations are shown or further discussed in this thesis.

Discussion of Results

From Figure 2, "The Plot of Extramolecular Contributions *vs.* the Reduced Temperature, θ," it may be seen that the values for the non-linear polyatomic liquids are grouped, roughly, about the same curve. The linear molecular liquid, carbon disulfide, follows a different, lower-valued curve.

Bhagavantam[22] has shown that the extramolecular contribution to the heat capacity of liquid benzene approaches .12 cal/mole-°K, the

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[22] S. Bhagavantam, *loc. cit.*

maximum value for an ideal non-linear molecular solid, near the melting point. The extramolecular contributions of ethylene dichloride and ethylene dibromide, in Figure 2, extend this result for molecular liquids.

The results for n-heptane, in Figure 2, indicate that for this liquid the extramolecular contribution near the melting point is greater than 12 cal/mole-°K, but C_v from which the values for n-heptane were determined were calculated from compressibilities extrapolated over a considerable temperature range; consequently, the results near the melting point may not represent the true curve for this liquid.

In general, the slope of the curves for the other non-linear liquids examined tend to confirm the trend towards the 12 calorie value at the melting point; however, the data were not extensive enough to confirm this trend with certainty. The slope of the curve for fluorobenzene is somewhat greater than that for the curves of the other liquids examined, but the results for fluorobenzene were calculated from estimated gas heat capacities (Appendix III) which may have been enough in error to cause the slope of the $C_v - C_i$ curve for fluorobenzene to be too steep.

The results for acetone were slightly higher than those for the other non-linear liquids examined. This may arise from the fact that acetone is more highly associated in the liquid state.

Discussion of the Non-Linear Liquids (Figure 3)

In order to facilitate the comparison of $C_v - C_i$ between polyatomic and monatomic liquids, the results for both were replotted on

the same graph. This plot is shown in Figure 3 and should be referred to for the remainder of this discussion.

The lower solid curve of Figure 3 is the curve of Bauer, Magat, and Surdin for monatomic liquids. The upper solid curve is exactly parallel with and 6 cal/mole-°K higher than the lower solid curve and is shown in order to further facilitate comparison of the plot of polyatomic liquids with the latter.

The broken curve is the mean of the results for the non-linear polyatomic liquids, except carbon tetrachloride. The agreement between the values at corresponding reduced temperatures for the different liquids examined, except carbon tetrachloride, is well within the indeterminancy of the results. The curve for carbon tetrachloride is lower and of steeper slope than any of the others. A probable explanation for this fact is offered below.

If it be assumed that the curve for monatomic liquids represents the contribution of translation in the liquid state, the distance between this curve and the dotted mean curve may be taken to measure the rotational contribution. Assigning the value, 6 cal/mole-°K, to completely restricted rotation and the value, 3 cal/mole-°K, to completely free rotation, one may see that, for the liquids here examined, rotation is considerably restricted at values of θ less than 0.5. The trend of the mean curve above $\theta = 0.3$ indicates a rapid approach to free rotation at higher temperatures. The data here are not extensive enough, however, to indicate whether or not this condition is actually reached in the liquid state.

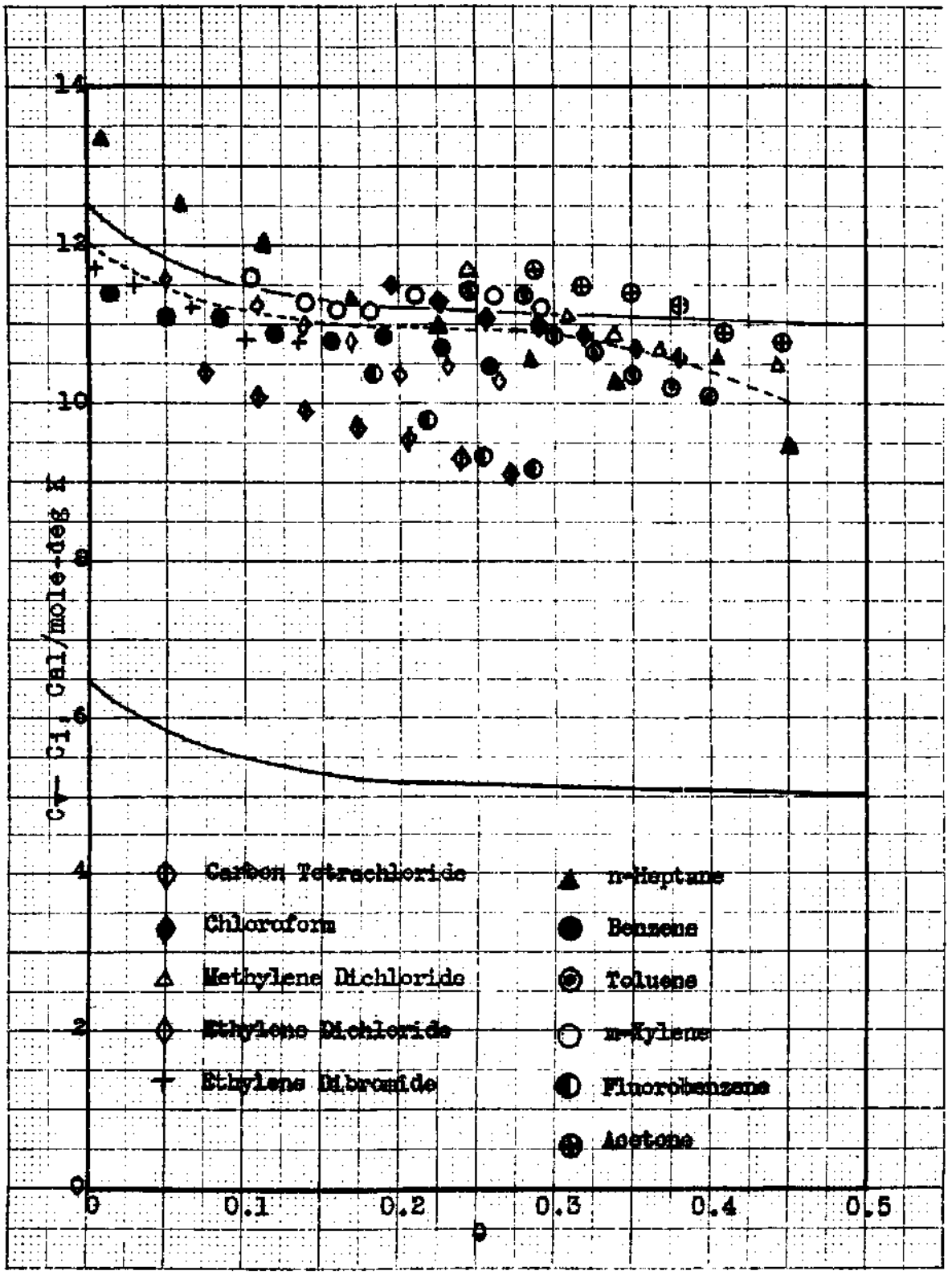

Figure 3. Plot of Extramolecular Contributions vs. Reduced Temperatures for Non-Linear Molecular Liquids

The results for carbon tetrachloride probably indicate less restriction of rotation initially and a faster, more nearly linear, approach to free rotation than in the case of the other liquids examined, apparently reaching free rotation at a value of θ less than 0.5. It is suggested that this occurs because of the greater symmetry of the carbon tetrachloride molecule.

In this connection it was noted that a rotational type transition occurs in the heat capacity curve for solid carbon tetrachloride. Hicks, Hooley, and Stephenson[23] have reported the transition at 225.35°K $\pm$ 0.03°K; Δ H transition = 1095 $\pm$ 3 cal/mole, and, Δ S transition = 4.859 eu. Fusion is at 250.35°K; Δ H fusion = 601 $\pm$ 2 cal/mole, and, Δ S fusion = 2.401 eu. Stull[24] reported this transition at 225.63°K, and, Δ H transition = 1100 cal/mole.

Railing[25] and Pitzer[26] have reported transitions in the heat capacity curves of solid ethylene dichloride and ethylene dibromide. Railing suggested the transition in the chloride is due to zigzag rotation about the x-c-c-x axis, and stated that the dielectric constant

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[23] J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson, "The Heat Capacity of Carbon Tetrachloride from 15 to 300°K. The Heats of Transition and Fusion. The Entropy from Thermal Measurements Compared with the Entropy from Molecular Data," J. Am. Chem. Soc., 66: 1064-1067, 1944.

[24] D. R. Stull, "A Semi-Micro Calorimeter for Measuring Heat Capacities at Low Temperatures," J. Am. Chem. Soc., 59: 2726-2733, 1937.

[25] W. E. Railing, "The Specific Heats of Some Ethylene Halides," J. Am. Chem. Soc., 61: 3349-3353, 1939.

[26] K. S. Pitzer, "The Heat Capacities, Heats of Transition and Fusion, and Entropies of Ethylene Dichloride and Ethylene Dibromide," J. Am. Chem. Soc., 62: 331-335, 1940.

is unaffected in the region of the hump. Pitzer has pointed out that the setting in of rotation about the long axes of the molecules might explain the results for each substance by itself but not the great difference for two such similar compounds. He has proposed the following explanation but stated that it was by no means proved.

> "If cooperative (coupling) effect between the rotation of one molecule and its neighbors is relatively small, then the whole curve for the chloride becomes understandable. The gradual rise for the bromide curve from 150 to 250°K is also expected. Above 250°K some fundamentally different crystal structure based on rotating molecules becomes more stable for the ethylene dibromide and a sharp interphase transition of the usual sort occurs."

Pitzer also proposed that the lattice for ethylene dichloride is essentially the same above and below the peak, and, that the lattice below the transition is also similar for ethylene dibromide but quite different above the transition. According to Pitzer, extra entropy due to the transition is 2.8 eu for ethylene dichloride and 3.7 eu for ethylene dibromide, the latter being the larger because it includes the lattice change in addition to molecular rotation.

If these transitions involved overall rotation of the molecules (rather than internal rotation) as suggested by Railing and Pitzer, it cannot be explained by the analysis attempted in the present work why the extramolecular contributions to heat capacity for these two liquids do not follow the curve for carbon tetrachloride instead of the mean curve in Figure 3.

It is, however, to be noted that the points for ethylene dichloride, ethylene dibromide, and benzene are consistently lower than

the others. This trend might be explained as follows:[27]

For benzene, rotation in the plane of the ring would be quite easy due to the high symmetry (⬡) . This rotation is not possible in toluene or m-xylene because of reduced symmetry (but it should be possible for methylene dichloride -- the hydrogen bounding may also be important in this case).

For ethylene dichloride and ethylene dibromide, the internal heat capacity, C_i, is abnormally high because of the unusual potential function used to calculate the contribution due to internal rotation (Appendix III, Figure 11. The contribution due to internal rotation amounts to 3.8 cal/mole-°K). In the liquid, this potential may not be so unusual, but may be more like a usual cosine term with a maximum in C (I. Rot.) of 2 cal/mole-°K. Values of C_i for these substances in the liquid state may, therefore, be overcorrected.

Linear Molecular Liquids

The foregoing analysis of the heat capacity of liquids consisting of non-linear molecules should also be applicable to those consisting of linear molecules, except that five instead of six degrees of freedom are extramolecular. Consequently, near the melting point the extramolecular heat capacity of linear molecules might be expected to approximate 10 cal/mole-°K unless the rotation about the two short axes is completely free; in which case it might be expected that the extramolecular contribution would approximate 8 cal/mole-°K.

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[27]Appreciation is expressed to Dr. W. H. Eberhardt for the suggestions incorporated in these paragraphs.

According to the results of Bauer, Magat, and Surdin (Figure 1), the latter seems to be the case for the diatomic liquids, bromine and air. As pointed out above, however, the portion of the curve between $\theta=0$ and $\theta=0.21$, drawn through the C_v of bromine, does not represent the extramolecular contribution in the sense of this thesis, since it includes from 1.5 to 1.7 cal/mole-°K due to the absorption of energy by the internal molecular vibration. If this be subtracted from the curve for bromine, the extramolecular contribution at the melting point is 7.5 and at $\theta=0.2$ is 6.3. This still roughly approximates the expected result, but is, however, somewhat lower than expected. If this be done, the curve for bromine appears somewhat lower than the curve for air.

The only linear molecular liquid examined was carbon disulfide. The extramolecular contributions for this liquid were plotted with the curves of extramolecular contributions for diatomic and monatomic liquids as determined from the results of Bauer, Magat, and Surdin. The vibrational contributions for bromine were subtracted from C_v as indicated above. This plot is shown in Figure 4. The five points for which data were available for carbon disulfide fall almost exactly on the curve for air. This curve is everywhere approximately 2.5 cal/mole-°K higher than the curve for monatomic liquids. If the assumption be made that the curve for monatomic liquids represents, in general, the translational contribution for molecular liquids, the 2.5 cal/mole-°K difference indicates practically free rotation of the molecules in liquid carbon disulfide as well as in the diatomic liquids air and bromine.

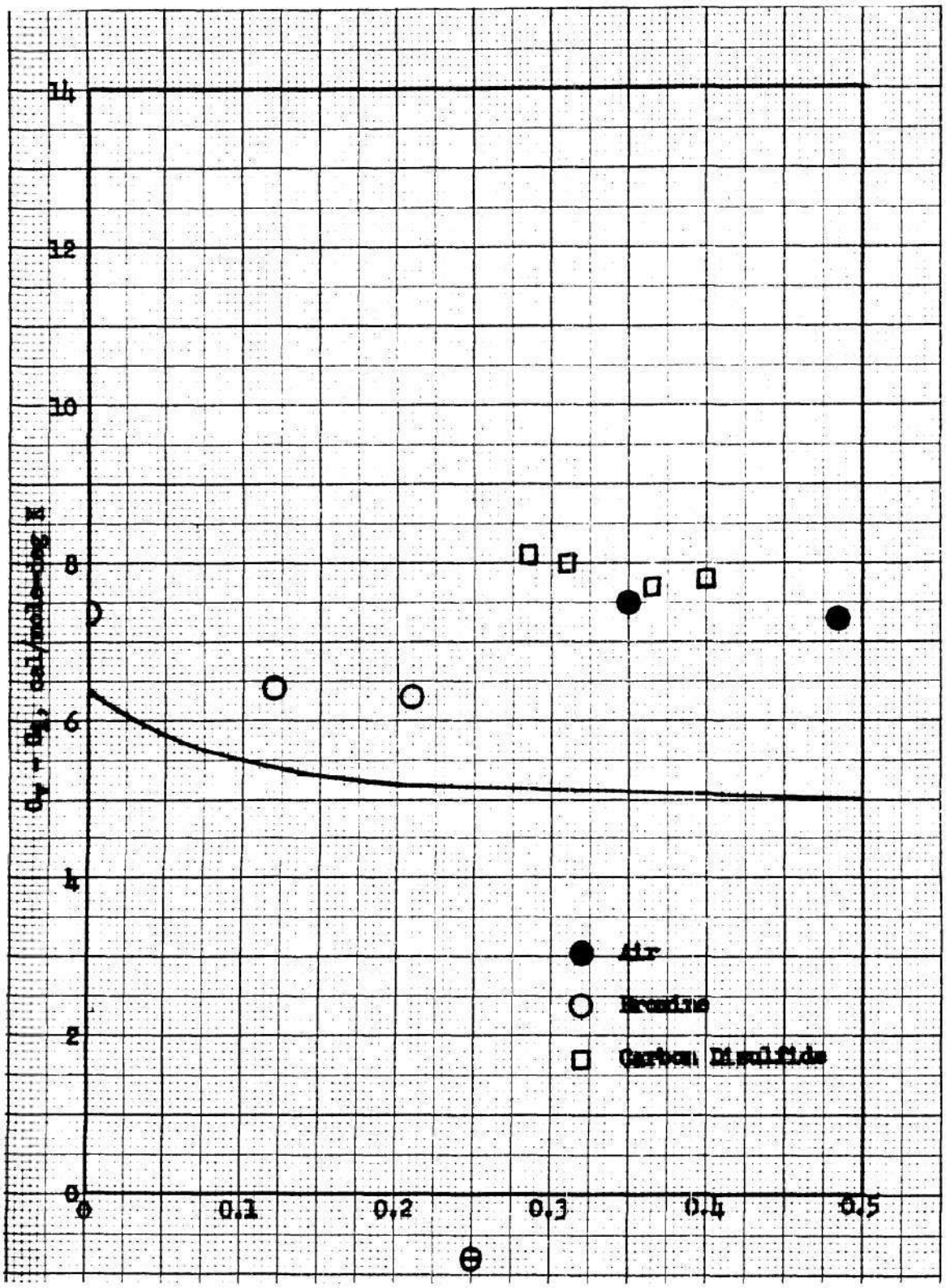

Figure 4. Plot of Extramolecular Contributions vs. Reduced Temperatures for Linear Molecular Liquids

Estimation of the Heat Capacities of Liquids

The heat capacity at constant volume of a molecular liquid may be estimated by adding an extramolecular contribution chosen from the curve of Figure 3 (or Figure 4, if the liquid is linear-molecular) to the internal contribution at the corresponding temperature. The latter may be determined from the internal vibration frequencies of the molecule or calculated from C_p^0 data for the gas, whichever is available.

If sufficient additional data for the liquid are known, the heat capacity at constant pressure may then be calculated. The procedure is given in the following equations:

$$C_p = (C_p - C_v) + C_v$$

$$= (C_p - C_v) + (C_v - C_i) + C_i$$

$$= (C_p - C_v) + (C_v - C_i) + (C_p^0 - 4R) \text{ non-linear molecular liquid}$$

$$= (C_p - C_v) + (C_v - C_i) + (C_p^0 - 7R/2) \text{ linear molecular liquid}$$

$(C_v - C_i)$ is the extramolecular contribution from Figure 3 or 4, and C_p^0 is the zero pressure gas heat capacity.

$(C_p - C_v)$ may be calculated by the method given in Chapter II. If the density and/or compressibility data necessary are unknown, they may be estimated by the method of Bauer, Magat, and Surdin,[28] who have correlated these data with their reduced temperature, Θ, for a number of liquids.

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[28] E. Bauer, M. Magat, and M. Surdin, loc. cit.

Some idea of the accuracy to be expected in the estimate of an unknown liquid heat capacity at constant pressure may be obtained by testing the worst case in Figure 3. The greatest deviation from the mean curve of Figure 3, except for carbon tetrachloride, which does not follow the mean curve as discussed in Chapter IV, occurs in the case of methylene dichloride at the reduced temperature, $\theta = 0.245$. For methylene dichloride at this reduced temperature the experimental extramolecular contribution is 0.75 cal/mole-°K removed from the mean curve and the experimental heat capacity at constant pressure is 23.35 cal/mole-°K. Assuming all other data to be accurate, the error in the estimated heat capacity is 0.75 x 100/23.35, or 3.3 per cent.

For carbon tetrachloride at 333.2°K, the error in the heat capacity estimated from the mean curve of Figure 3 would be 6.3 per cent. In order to assure that this deviation for carbon tetrachloride was not caused by errors in compressibility or density data, and therefore could be considered to represent a fundamentally different behavior of the molecules in carbon tetrachloride liquid, these data for carbon tetrachloride were examined in considerable detail and K_T calculated in the present work was compared with K_T calculated in other papers. The results of this comparison are shown in Table V of Appendix II.

The greatest difference between the K_T calculated in this thesis and K_T from another source occurred at 273.2°K. The calculation in this thesis, based on $K_S = 62.0 \times 10^{-6}$ (taken from a best curve drawn through data from several sources) gave $K_T = 89.3 \times 10^{-6}$ atm^{-1}

and $C_v = 21.70$ cal/mole-°K. C_v based on compressibilities from the International Critical Tables[29] ($K_S = 62 \times 10^{-6}$ megabyres$^{-1} = 63.82 \times 10^{-6}$ atm^{-1} and $K_T = 90 \times 10^{-6}$ megabyres$^{-1} = 91.2 \times 10^{-6}$ atm^{-1}) is 21.53 cal/mole-°K. The difference between the results of these two calculations for C_v is, therefore, 0.17 cal/mole-°K or 0.8 per cent. Assuming an error of one per cent due to compressibility and density data used cumulative with a one per cent error due to the C_p used, the error in C_v still is not large enough to account for the deviation of the curve for carbon tetrachloride in Figure 3.

Table III, which follows, lists the normal melting points and critical temperatures of the liquids examined in this thesis, together with the calculated reduced temperatures, θ, and corresponding extramolecular contributions to heat capacity, $C_v - C_i$, used in the preparation of Figures 2 through 4.

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[29] International Critical Tables of Numerical Data, Physics, Chemistry and Technology, First Edition (New York: McGraw-Hill Book Co., Inc., National Research Council, 1930), p. 39.

TABLE III

RESULTS OF CALCULATIONS FOR REDUCED TEMPERATURES*

Liquid	T °K	θ*	$C_v - C_i$ cal/mole-°K	Liquid	T °K	θ*	$C_v - C_i$ cal/mole-°K
Carbon Tetrachloride T_c 556.3°K T_f 250.4°K	273.2	0.0745	10.4	Chloroform T_c 533.2°K T_f 209.7°K	273.2	0.196	11.5
	283.2	0.107	10.1		283.2	0.227	11.3
	293.2	0.140	9.9		293.2	0.258	11.1
	303.2	0.173	9.7		303.2	0.289	11.0
	313.2	0.205	9.5		313.2	0.320	10.9
	323.2	0.238	9.3		323.2	0.351	10.7
	333.2	0.271	9.1		333.2	0.382	10.6
Methylene Dichloride T_c 489°K T_f 176.4°K	253.2	0.245	11.7	Ethylene Dichloride T_c 561.6°K T_f 237.9°K	253.2	0.0474	11.6
	273.2	0.309	11.2		273.2	0.109	11.3
	283.2	0.341	10.9		283.2	0.140	11.0
	293.2	0.371	10.8		293.2	0.171	10.8
	303.2	0.405	10.7		303.2	0.202	10.4
	313.2	0.437	10.6		313.2	0.233	10.5
	323.2	———	———		323.2	0.264	10.3
Carbon Disulfide T_c 546.2°K T_f 161.4°K	273.2	0.288	8.1	Ethylene Dibromide T_c 583.0°K T_f 283.2°K	283.2	0.000	11.7
	283.2	0.314	8.0		293.2	0.0334	11.5
	293.2	0.340	7.8		303.2	0.0668	11.2
	303.2	0.366	7.7		313.2	0.100	10.8
	313.2	0.392	7.7		323.2	0.134	10.8
Acetone T_c 508.2°K T_f 178.9°K	273.2	0.286	11.6	Fluorobenzene T_c 559.7°K T_f 231.1°K	293.2	0.189	10.4
	283.2	0.318	11.5		303.2	0.219	9.8
	293.2	0.348	11.4		313.2	0.250	9.3
	303.2	0.378	11.2		323.2	0.280	9.0
	313.2	0.408	10.9		333.2	———	———
	323.2	0.439	10.6		343.2	———	———

(continued on next page)

TABLE III
(continued)

Liquid	T °K	θ*	$C_v - C_i$ cal/mole-°K	Liquid	T °K	θ*	$C_v - C_i$ cal/mole-°K
	283.2	0.016	11.4		283.2	0.253	11.7
	293.2	0.051	11.1		293.2	0.277	11.4
Benzene	303.2	0.086	11.1	Toluene	303.2	0.301	10.9
	313.2	0.121	10.9		313.2	0.325	10.7
T_c 562.7°K	323.2	0.157	10.8	T_c 593.8°K	323.2	0.349	10.4
T_f 278.7°K	333.2	0.192	10.9	T_f 178.2°K	333.2	0.373	10.3
	343.2	0.227	10.7		343.2	0.397	10.1
	353.2	0.262	10.3		353.2	———	———
	273.2	0.113	11.6		183.2	0.002	13.4
	283.2	0.137	11.3		203.2	0.058	12.6
	293.2	0.161	11.2		223.2	0.114	12.0
m-Xylene	303.2	0.185	11.2	n-Heptane	243.2	0.170	11.3
	313.2	0.208	11.4		263.2	0.226	11.0
T_c 645°K	323.2	0.232	11.4	T_c 540°K	283.2	0.282	10.5
T_f 225.8°K	333.2	0.256	11.5	T_f 182.5°K	303.2	0.338	10.3
	343.2	0.280	11.3		323.2	0.394	10.1
	353.2	0.304	11.6		343.2	0.450	9.4
	363.2	———	———		363.2	0.506	8.6

* T - Absolute Temperature: degrees Kelvin.
T_f - Temperature of Freezing: degrees Kelvin.
T_c - Critical Temperature: degrees Kelvin.
θ - Reduced Temperature, $\frac{T - T_f}{T_c - T_f}$: dimensionless.

$C_v - C_i$ - The Intermolecular Contribution to Heat Capacity of the Liquid: calories/mole-degrees Kelvin.

APPENDICES

APPENDIX I

HEAT CAPACITY DATA FOR LIQUIDS

This appendix shows the choice of C_p used in the calculations of C_v in Chapter II. Each liquid is treated individually in the following discussions and plots. The estimate made in Chapter II that C_p for each of the liquids are accurate within one per cent was based on these plots and discussions.

Carbon Tetrachloride

Values for C_p used in the calculation of C_v for carbon tetrachloride were taken from the curve of Figure 5 drawn through measurements of Hicks, Hooley, and Stephenson,[30] Stull,[31] Williams and Daniels,[32] Mills and MacRae,[33] Richards and Wallace,[34] and of Vold.[35] All the data except the two extreme points of Williams and Daniels agree within 1.5 per cent with each other and within one per cent with the curve drawn.

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[30] J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson, loc cit.

[31] D. R. Stull, loc. cit.

[32] J. W. Williams and F. Daniels, "The Specific Heats of Certain Organic Liquids at Elevated Temperatures," J. Am. Chem. Soc., 46:903-917, 1924.

[33] J. E. Mills and D. MacRae, "Specific Heat of Carbon Tetrachloride," J. Phys. Chem., 15: 54-66, 1911.

[34] W. T. Richards and J. H. Wallace, Jr., "The Specific Heats of Five Organic Liquids from Their Adiabatic Temperature-Pressure Coefficients," J. Am. Chem. Soc., 54: 2705-2713, 1932.

[35] R. D. Vold, "A Calorimetric Test of the Solubility Equation for Regular Solutions," J. Am. Chem. Soc., 59: 1515-1521, 1937.

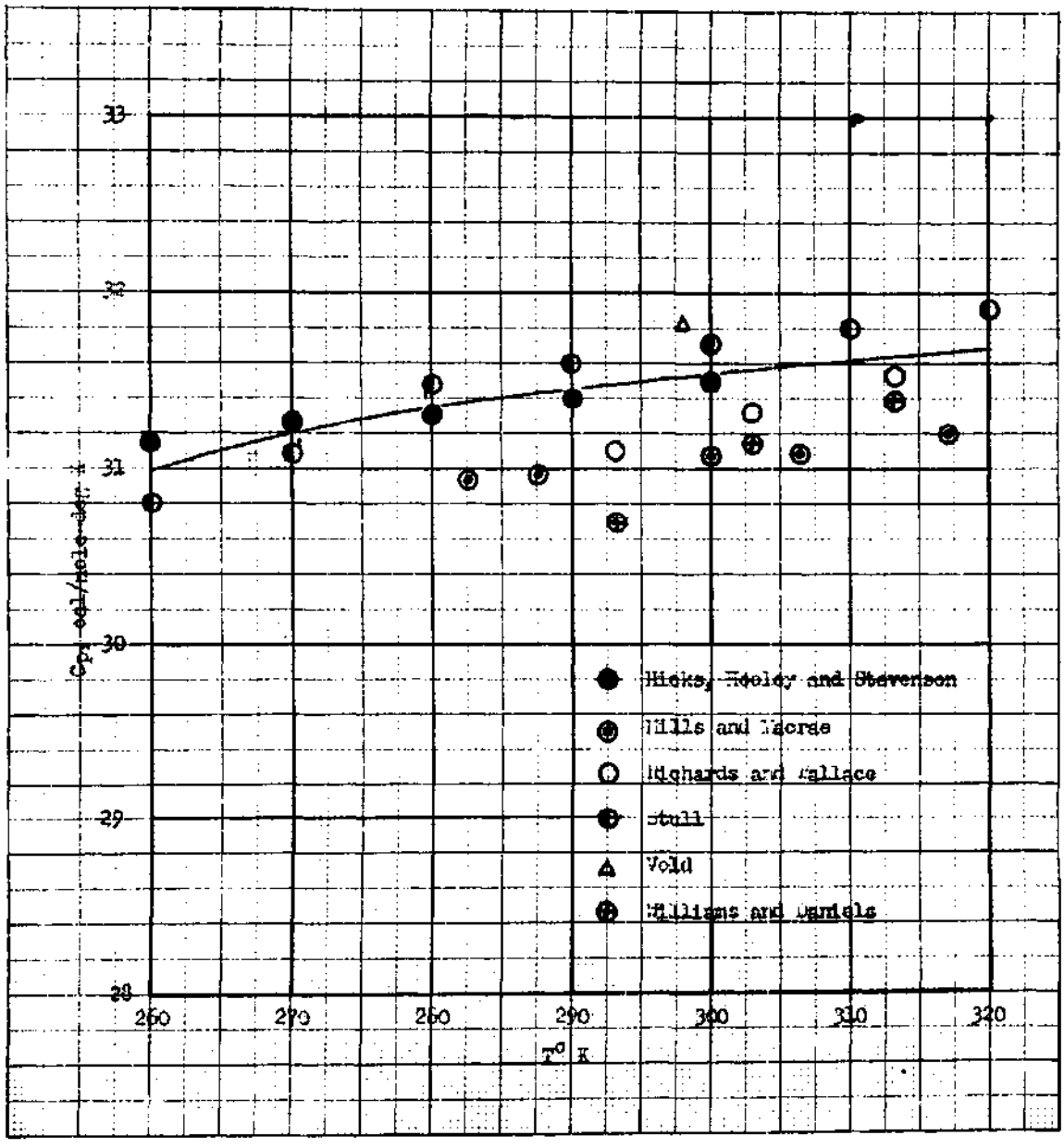

Figure 5. Heat Capacity of Liquid Carbon Tetrachloride

Bhagavantam[36] has calculated the C_v of carbon tetrachloride from the C_p data of Mills and MacRae and of Williams and Daniels. Since their measurements are lower than the average curve of Figure 5, Bhagavantam's results for C_v are slightly lower than those calculated in Chapter II of this thesis.

Carbon Disulfide

Values used in the calculations for carbon disulfide were taken from the "best curve", Figure 6, drawn through the measurements of Regnault,[37] Shulze,[38] Hirne,[39] and of Brown and Manov.[40] This curve lies within one per cent of all the data. The upper range of Brown and Manov's low temperature determinations agrees well with the lower range of Regnault's measurements, whereas, the upper range of Regnault's work shows very good agreement with the high temperature

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[36] S. Bhagavantam, loc. cit.

[37] H. Regnault, Mem. de l'Acad. Royale des Sciences de l'Institute France, 26: 262, 1862.

[38] A. Shulze, "Die Spezifishe Warme Binarer Gemische I," Verhandlungen der Phys. Gesellchaft zu Berlin, 14: 189, 1912.

[39] G. A. Hirn, "Memoire sur la Thermodynamique, I. Recherches Experimentales sur la Dilatation et sur la Capacite Calorifique, a de Hautes Temperatures de Quelques Liquides Tres-Volatils," Annales de Chemie et de Physique, 10: 32-92, 1867.

[40] O. L. I. Brown and G. G. Manov, "The Heat Capacity of Carbon Disulfide from 15° to 300°K. Entropy and Heat of Fusion," J. Am. Chem. Soc., 59: 500-502, 1937.

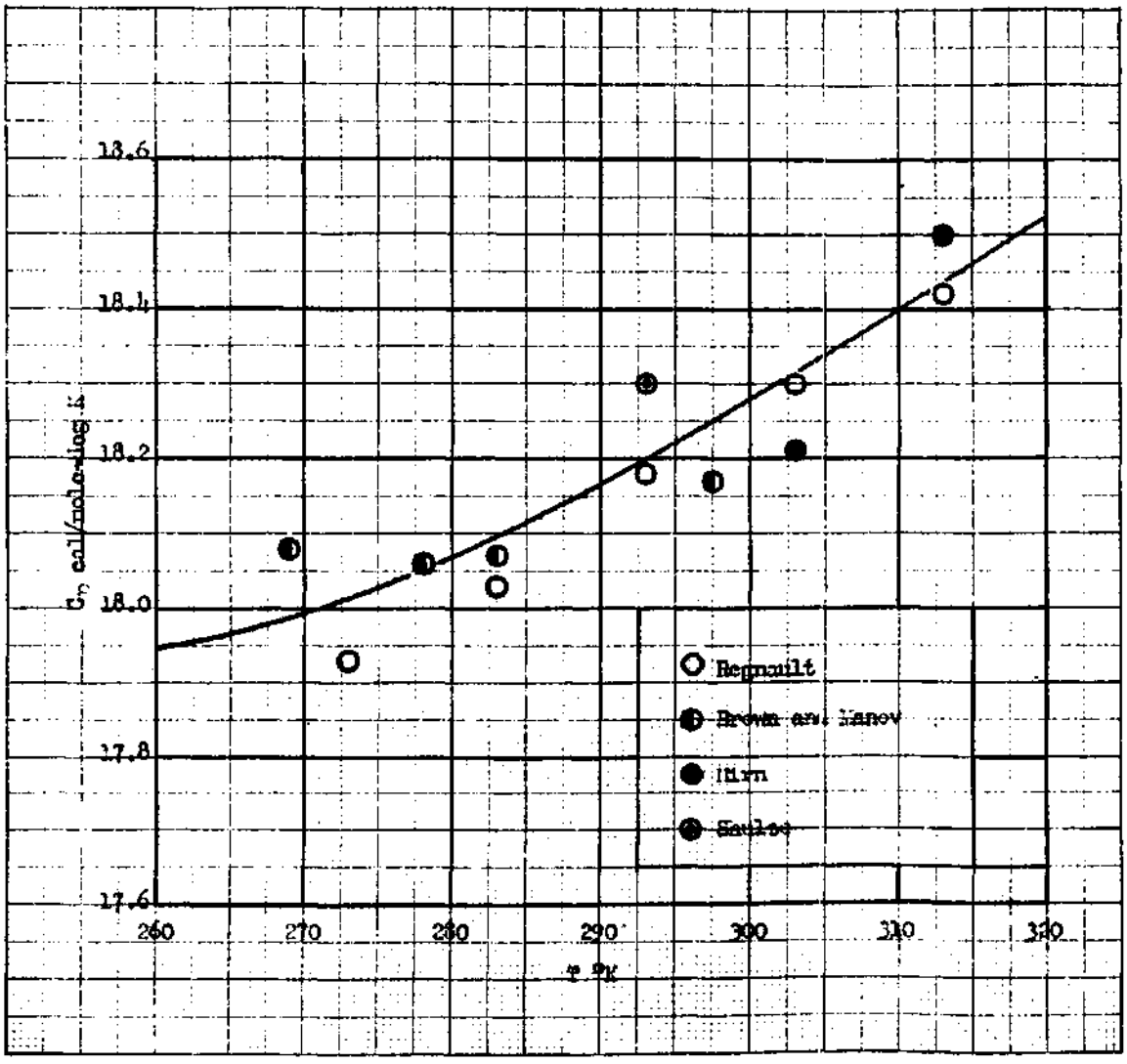

Figure 6. Heat Capacity of Liquid Carbon Disulfide

determinations of Hirn. Sutherland[41] has shown that a recalculation of Hirn's results will give values in even closer agreement with the work of Regnault. Determinations at single temperatures made by Forch[42] and by Hartung[43] were disregarded since each varies from the work of the other investigators by three per cent.

Chloroform

Values used in the calculations for this liquid were taken from the "best curve", Figure 7, drawn through the measurements of Regnault,[44] Trehin,[45] Shulze,[46] Williams and Daniels,[47] and of Kurbatov.[48]. This curve is shown in Figure 7. The agreement of all the data is within one per cent of the mean except at the upper and lower extreme temperatures where the agreement is about 1.5 per cent.

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[41] W. Sutherland, "On the Recalculation of Certain Specific Heats at High Temperatures and the Specific Heat of Water," Phil. Mag. and Jour. Sci., 26 (5): 298-305, 1888.

[42] C. Forch, "Die Spezifishe Warme des Losungen von Naphthalin in Verschiedenen Organischen Losungsmitteln," Ann. Physik, 12: 202, 1903.

[43] E. J. Hartung, Trans. Fara. Soc., May 11, 1915.

[44] H. Regnault, loc. cit.

[45] R. Trehin, "Chaleurs Specifique de Quelques Liquides Organiques," Annales de Physique, 15: 246-263, 1921.

[46] A. Shulze, loc. cit.

[47] J. W. Williams and F. Daniels, "The Specific Heats of Binary Mixtures," J. Am. Chem. Soc., 47: 1490-1503, 1925.

[48] V. Ya. Kurbatov, "Heat Capacities of Liquids II. Temperature Dependence of the Heat Capacity of Halogen Derivatives of Acylic Hydrocarbons," Zhur. Obishchei Khim., 18: 372-387, 1948 (Chemical Abstracts, 43: 30c, 1949).

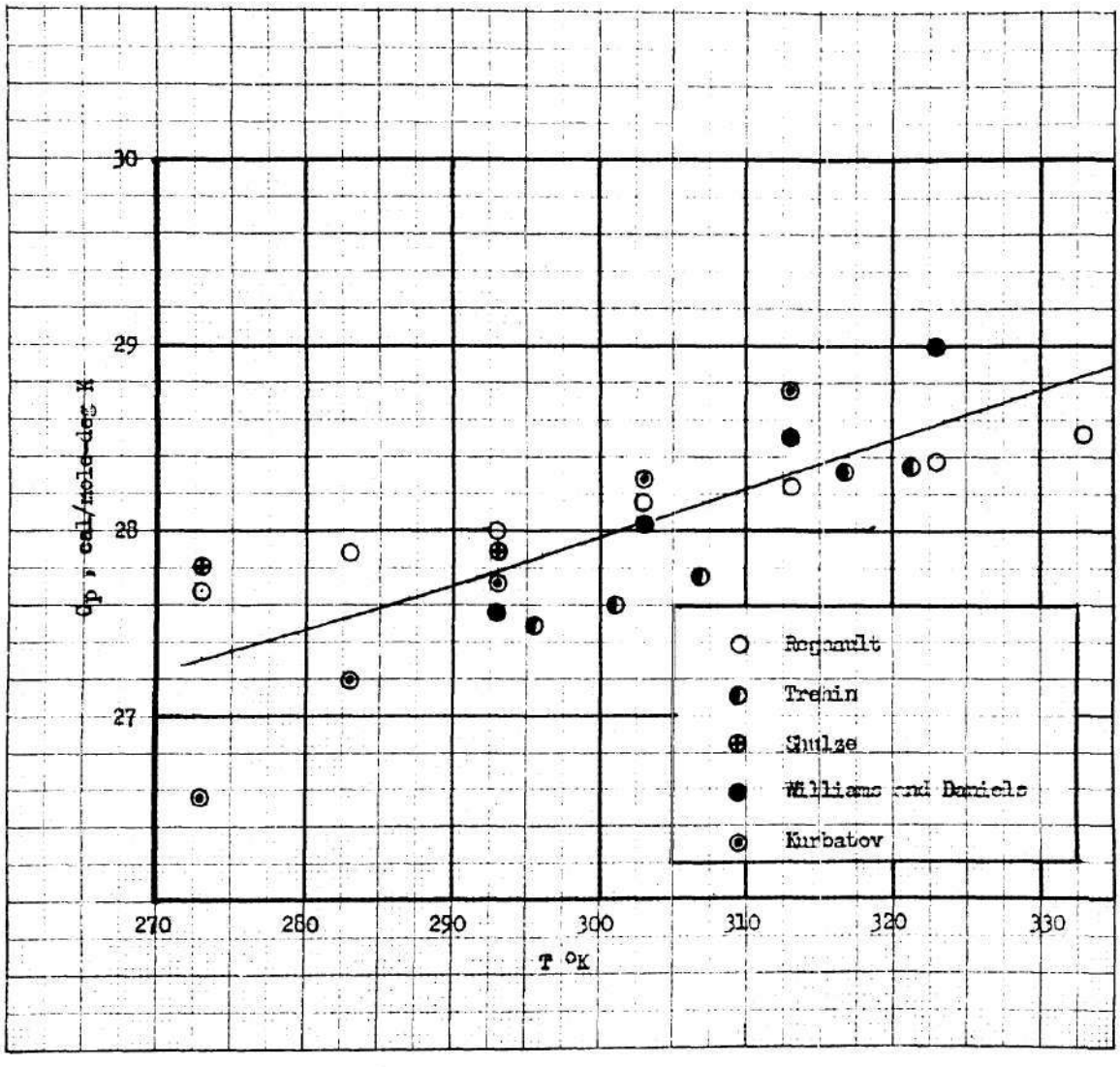

Figure 7. Heat Capacity of Liquid Chloroform

Methylene Chloride

Dzung[49] has critically examined the heat capacity data available for methylene chloride and chosen the work of Perlick[50] and of Riedel[51] as being fairly accurate. He has given the following equation for the specific heat of the saturated liquid:

$$C_p = 0.276 + 0.12 \times 10^{-3} t + 3.0 \times 10^{-6} t^2 .$$

Accuracy: one per cent between -50°C and 40°C.

Since a survey of the literature revealed no other liquid heat capacity data, values used in these calculations were taken from this equation.

Ethylene Dichloride

Pitzer[52] and Railing[53] have measured the heat capacity of liquid ethylene dichloride. The results of Pitzer were, for the most part, about 0.5 cal/mole-°K lower than those of Railing. Railing has

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[49] L. S. Dzung, "Thermodynamic Properties of Methylene Chloride," The Brown Boveri Review, 158-163, June-July, 1946.

[50] A. Perlick, "Kalorimetrische Messungen an Schwefeldioxyde, Methylenchlorid, Difluormonochlorathan und Tetrafluordichlorathan," Zeitschrift fur die gesamte Kalteindustrie, 44: 201, 1937.

[51] L. Riedel, "Bestimmung der spezifischen Warme von Athylchlorid und Methylenchlorid in flussigem Zustand," Zeitschrift fur die gesamte Kalteindustrie, 47: 87, 1940.

[52] K. S. Pitzer, "The Heat Capacities, Heats of Transition and Fusion, and Entropies of Ethylene Dichloride and Ethylene Dibromide," J. Am. Chem. Soc., loc. cit.

[53] W. E. Railing, loc. cit.

stated that his results are about 2 calories lower than previously published data but that these data are from 40 to 75 years old.

C_p values used in the calculations of Chapter II were chosen from the results of Pitzer because it was believed that his method of measurement is somewhat more reliable than the method used by Railing. This belief was based on the discussion of the two methods in Pitzer's paper.

Ethylene Dibromide

Pitzer,[54] Railing,[55] and Kurbatov[56] have reported heat capacity measurements for ethylene dibromide. Their data are compared in Figure 8. Pitzer's results agree within one to two per cent with those of Railing but do not confirm the dip in Railing's curve. Kurbatov's curve is much steeper than Pitzer's. The three higher temperature determinations of Railing (just past the minimum of his curve) are parallel with Kurbatov's curve but about one calorie lower than Kurbatov's corresponding points, being in fair agreement with the measurements of Pitzer.

It was believed that the measurements of Pitzer are the more reliable; consequently, his results were adopted for use in Chapter II.

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[54] K. S. Pitzer, "The Heat Capacities, Heats of Transition and Fusion, and Entropies of Ethylene Dichloride and Ethylene Dibromide," J. Am. Chem. Soc., loc. cit.

[55] W. E. Railing, loc. cit.

[56] V. Ya. Kurbatov, op. cit., p. 30 a,e.

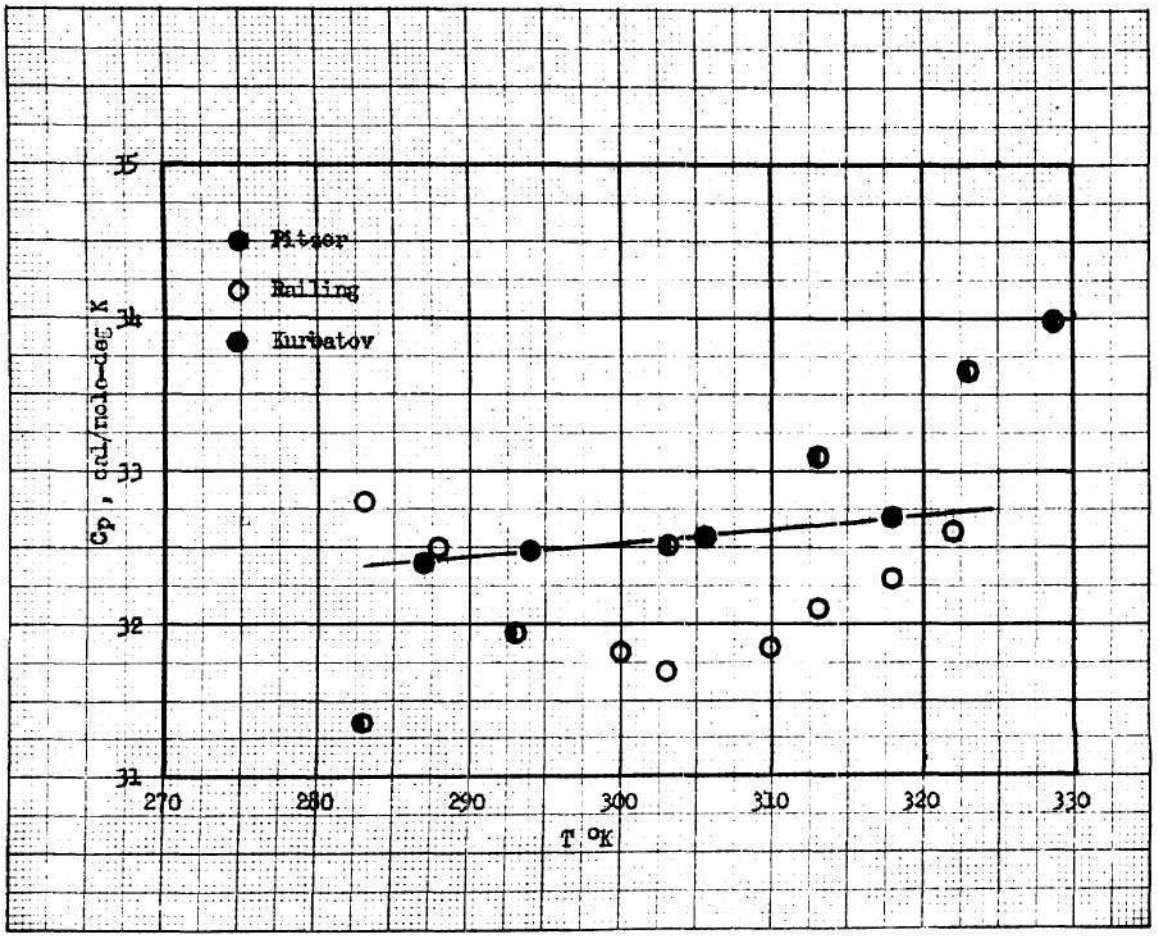

Figure 8. Heat Capacity of Liquid Ethylene Dibromide

n-Heptane

Measurements of Pitzer,[57] Parks, Huffman, and Thomas,[58] Osborne and Ginnings,[59] Osborne, Stimson, and Ginnings, Williams and Daniels,[60] and of Richards and Wallace[61] were examined. The previously unpublished results of Osborne, Stimson, and Ginnings were reported in the paper of Osborne and Ginnings.

The numbers used in the calculations of Chapter II were taken from a "best curve" drawn through all the data of the above listed workers. Since the results of each of these investigators were well within one per cent of the mean curve, the comparative plot made of their data is not shown in this thesis.

Acetone

Values of C_p used in the calculations for acetone were taken from the smooth curve of Figure 9 drawn through the measurements of

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[57] K. S. Pitzer, "The Thermodynamics of n-Heptane and 2,2,4-Trimethylpentane, Including Heat Capacities, Heats of Fusion and Vaporization and Entropies," J. Am. Chem. Soc., loc. cit.

[58] G. S. Parks, H. M. Huffman, and S. B. Thomas, "Thermal Data on Organic Compounds: VI. The Heat Capacities, Entropies and Free Energies of Some Saturated, Non-Benzoid, Hydrocarbons," J. Am. Chem. Soc., 52: 1032-1041, 1930.

[59] N. S. Osborne and D. C. Ginnings, "Measurements of Heat of Vaporization and Heat Capacity of a Number of Hydrocarbons. III. Heat Capacity of Twelve Hydrocarbons," J. Research Natl. Bur. Stand., 39: 453-477, 1947 (Research Paper 1841).

[60] J. W. Williams and F. Daniels, "The Specific Heats of Certain Organic Liquids at Elevated Temperatures," J. Am. Chem. Soc., loc. cit.

[61] W. T. Richards and J. H. Wallace, Jr., loc. cit.

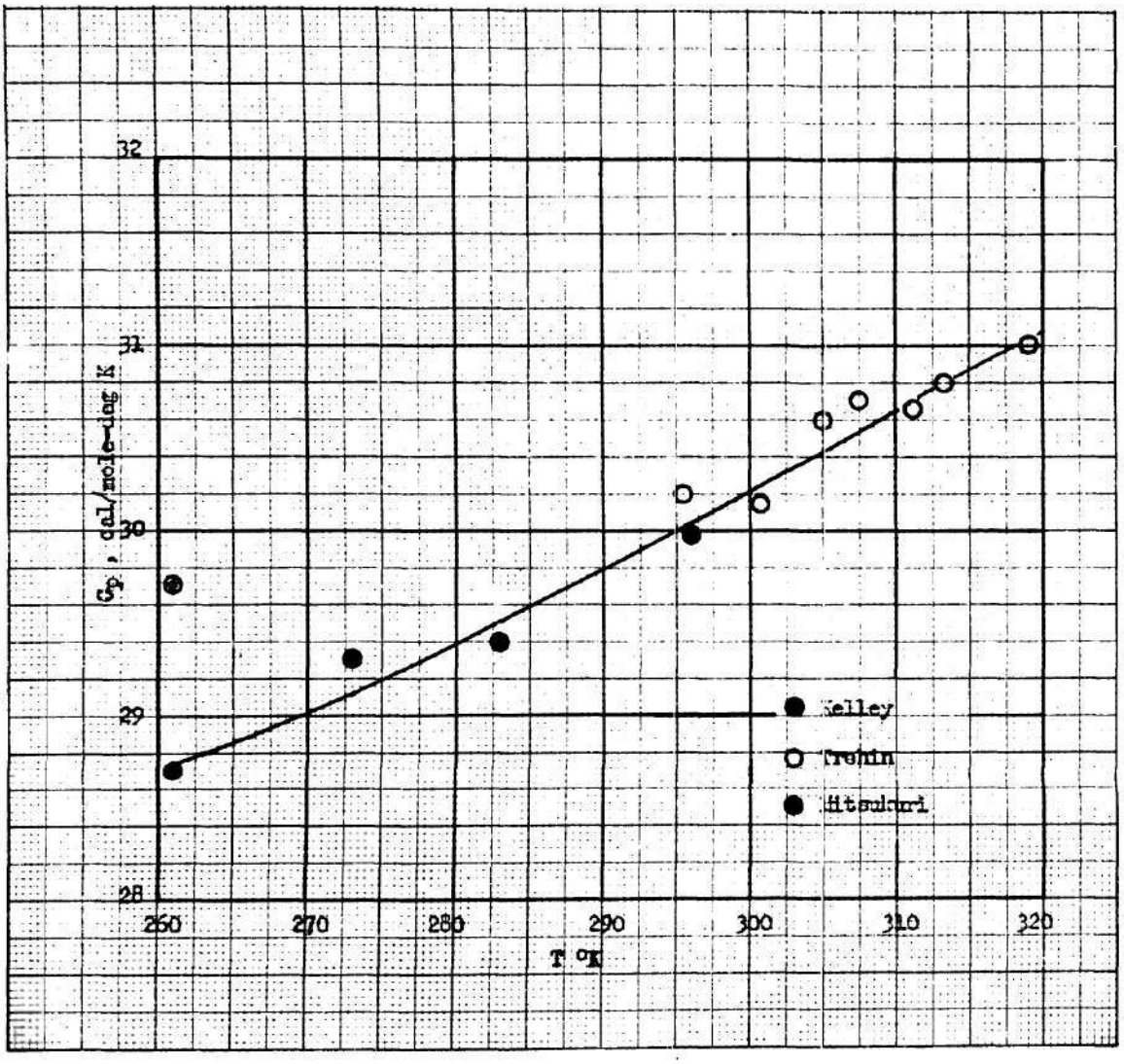

Figure 9. Heat Capacity of Liquid Acetone

Kelley[62] and of Trehin.[63] Results of Parks and Kelley[64] and of Mitsukuri and Hara[65] were also examined; but, were not included when making the choice of C_p values accepted; because, the later measurements of Kelley superseded the less accurate determinations of Parks and Kelley, and, only one measurement within the low temperature results of Mitsukri and Hara fell in the temperature range investigated in this thesis. The low temperature measurements of Kelley and the higher temperature measurements of Trehin complement each other perfectly. The 260°K determination of Mitsukuri and Hara is within 0.6 cal/mole-°K (two per cent) of Kelley's corresponding measurement.

Benzene

Calculations for benzene were based on the heat capacity determinations of Burlew.[66]

Burlew has measured the heat capacity of benzene from 8 to 80°C and has made a careful comparison of his results with other data

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[62] K. K. Kelley, "The Heat Capacities of Isopropyl Alcohol and Acetone from 16 to 298°K and the Corresponding Entropies and Free Energies," J. Am. Chem. Soc., 51: 1145-1150, 1929.

[63] R. Trehin, loc. cit.

[64] G. S. Parks and K. K. Kelley, "The Application of the Third Law of Thermodynamics to Some Organic Reactions," J. Phys. Chem., 32: 734, 1928.

[65] S. Mitsukuri and K. Hara, "Specific Heats of Acetone, Methyl --, Ethyl --, and n-Propyl-Alcohol at Low Temperatures," Bull. Chem. Soc. Japan (in English), 4: 77-81, 1929.

[66] J. S. Burlew, "Measurement of the Heat Capacity of a Small Volume of Liquid by the Piezo-Thermometric Method. III. Heat Capacity of Benzene and Toluene from 8 deg. C to the Boiling Point," J. Am. Chem. Soc., 62: 696-700, 1940.

in the literature. His values lie between those determined by other investigators and agree with most of them within one per cent.

Stull[67] and Ziegler and Andrews[68] have also plotted the data of various workers and drawn smooth curves through the mean. The heat capacities of Burlew agree closely with these smoothed values.

Toluene

Measurements of Burlew were also adopted for the calculations concerning this liquid. He has shown that his results for this liquid differ from the mean of all previous data by less than one per cent.

m-Xylene

Results of Williams and Daniels,[69] Huffman, Parks, and Daniels,[70] and of Kurbatov[71] were examined. The results of Williams and Daniels were presented as the equation

$$c_p = 0.3764 + 0.000812\ t \quad \text{cal/g-°C}$$

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[67] D. R. Stull, loc. cit.

[68] W. T. Ziegler and D. H. Andrews, loc. cit.

[69] J. W. Williams and F. Daniels, "The Specific Heats of Certain Organic Liquids at Elevated Temperatures," J. Am. Chem. Soc., loc. cit.

[70] H. M. Huffman, G. S. Parks, and A. C. Daniels, "Thermal Data on Organic Compounds. VII. The Heat Capacities, Entropies, and Free Energies of Twelve Aromatic Hydrocarbons," J. Am. Chem. Soc., 52: 1547-1558, 1930.

[71] V. Ya. Kurbatov, "Heat Capacities of Liquids. I. Heat Capacity of Benzene Hydrocarbons," J. Gen. Chem. (USSR), 17: 1999-2009, 1947 (Chemical Abstracts, 42: 4829h).

range 30 to 80°C, estimated precision 0.1 per cent; and those of Kurbatov as the equation

$$C_p = 41.37 + 0.11055\ t \quad \text{cal/mole-°K}$$

range 15.8 to 132.2°C, t being the temperature in degrees Celsius in each equation. These equations were plotted as broken and solid lines, respectively, in Figure 10; whereas, experimental points of Huffman, Parks, and Daniels were plotted.

The results of Williams and Daniels and of Kurbatov disagree by 2 cal/mole-°C near 30°C, the disagreement becoming greater with increasing temperature. The low temperature determinations of Huffman, Parks, and Daniels appear to confirm the low temperature range of Kurbatov's equation; therefore, the results of Kurbatov were accepted for use in the calculations of Chapter II. No other data were available to confirm the upper range of Kurbatov's equation, however, and it is possible that his curve is too steep.

Fluorobenzene

The heat capacity measurements of Stull[72] were used in the calculations for this liquid. No search was made for other data for this liquid.

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[72] D. R. Stull, loc. cit.

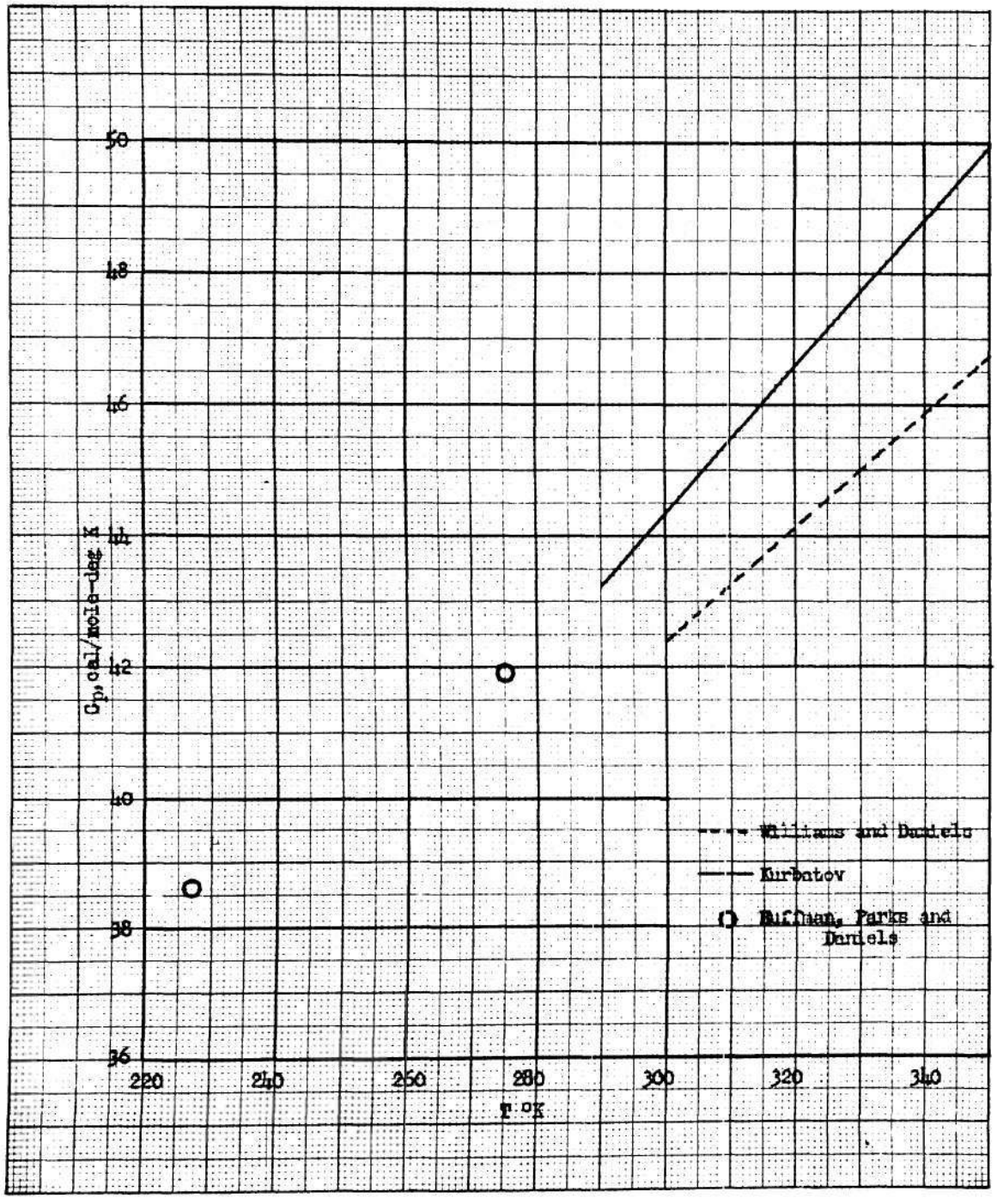

Figure 10. Heat Capacity of Liquid m-Xylene

APPENDIX II

COMPRESSIBILITY AND DENSITY DATA

Compressibility Data

The principal sources of compressibilities used in the calculations of C_v from C_p are the International Critical Tables,[73] and the papers of Tyrer,[74] Freyer, Hubbard, and Andrews,[75] and of Lagemann, McMillan, and Woolf.[76] The values reported in the International Critical Tables are essentially those of Tyrer.

Tyrer has made direct measurements of the adiabatic compressibilities; whereas, the latter workers have measured the velocities of sound in the liquids and calculated the adiabatic compressibilities therefrom. Lagemann, McMillan, and Woolf have recently determined sound velocities and calculated adiabatic compressibilities for several liquids for which these data were previously unknown.

The work of Freyer, Hubbard, and Andrews and of Lagemann, McMillan, and Woolf confirm the results of Tyrer wherever they have investigated the same liquid.

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[73] International Critical Tables, loc. cit.

[74] D. Tyrer, "Adiabatic and Isothermal Compressibilities of Liquids between One and Two Atmospheres Pressure," J. Chem. Soc., 105: 2534-2553, 1914.

[75] E. B. Freyer, J. C. Hubbard, and D. H. Andrews, "Sonic Studies of the Physical Properties of Liquids," J. Am. Chem. Soc., 51: 759, 1929.

[76] R. T. Lagemann, D. R. McMillan, Jr., and W. E. Woolf, "Temperature Variation of Ultrasonic Velocity in Liquids," J. Chem. Phys., 17: 369-373, 1949.

In cases where it has been possible to do so, the data from the principal sources have been compared with determinations of Gay,[77] Weissler,[78] Rao,[79,80] and Bhagavantam and Rao.[81] In each case, the agreement is good enough to justify the use of the principal source.

The adiabatic compressibilities used in the calculations for carbon tetrachloride are values from a "best curve" drawn through the results of Tyrer; Freyer, Hubbard, and Andrews; Lagemann, McMillan, and Woolf; and of Weissler. It is noted, however, that this procedure is not necessary, because of the very close agreement among the several workers, and is, therefore, not followed in the choice of compressibilities for the other liquids.

The absolute accuracy of the adiabatic compressibilities is not very important for the calculation of C_v. What is important is the accuracy of the ratio K_S/K_T, which is equal to the ratio C_v/C_p. Of prime importance, then, is the consistancy of the K_S with the K_T used in each case; this, in turn, depends upon the validity of the density and heat capacity data.

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[77] L. Gay, Comp. Rend., 156: 1978-1979 (Chemical Abstracts, 7: 3061[7], 1913).

[78] A. Weissler, "Ultrasonic Investigations of Molecular Properties of Liquids," J. Am. Chem. Soc., 71: 1272-1274, 1949.

[79] M. R. Rao, "Velocity of Sound in Liquids and Chemical Constitution," J. Chem. Phys., 9: 682-685, 1941.

[80] M. R. Rao, "The Adiabatic Compressibility of Liquids," J. Chem. Phys., 14: 699, 1946.

[81] S. Bhagavantam and Ch. V. Joga Rao, "Ultrasonic Velocity and Adiabatic Compressibility of Some Liquids," Proc. Indian Acad. Sci., 9A: 312-315, 1939.

The following Table IV, "Sources of Compressibilities," shows the principal and corraborative sources for the adiabatic and isothermal compressibilities used in the calculation of C_v for each liquid.

Lagemann, Evans, and McMillan[82] have reported the adiabatic compressibility of methylene dichloride at one temperature, 20° Celsius. They have, however, reported the sound velocities in this liquid at 10, 20, 30, and 40 degrees Celsius, and the adiabatic compressibilities were calculated in this thesis from these sound velocities. Table V shows this calculation.

Compressibilities from Extrapolated Sound Velocities

In several cases, where C_v has been calculated nearer the melting point than adiabatic compressibilities or sound velocities have been measured, namely: carbon tetrachloride at 263.2°K, methylene and ethylene dichloride at 253.2° and 273.2°K, and n-heptane below 273.2°K, linear extrapolations of the sound velocities have been made and adiabatic compressibilities calculated by the method illustrated in Table V for methylene dichloride. In view of the paper of Lagemann, McMillan, and Woolf,[83] it is believed that the results of these extrapolations for the organic halides listed above are very reliable.

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[82] R. T. Lagemann, J. S. Evans, and D. R. McMillan, Jr., "Ultrasonic Velocity in Some Organic Halides: Constitutive Effects," J. Am. Chem. Soc., 70: 2996-2999, 1948.

[83] R. T. Lagemann, D. R. McMillan, Jr., and W. E. Woolf, "Temperature Variation of Ultrasonic Velocity in Liquids," J. Chem. Phys., loc. cit.

TABLE IV

SOURCES OF COMPRESSIBILITIES*

Liquid	Adiabatic Compressibilities		Isothermal Compressibilities	
	Source of Values Used	Corraborative Sources	Source of Values Used	Corraborative Sources
Carbon Tetrachloride	"best curve"	Tyrer F,H, & A Weissler L,M & W	Calculated This Thesis	Tyrer F,H, & A
Carbon Disulfide	Tyrer	F,H, & A Gay B & R	Tyrer	F,H, & A
Chloroform	Tyrer	F,H, & A L,M, & W	Tyrer	F,H, & A
Methylene Dichloride	Calculated This Thesis	L,E, & M	Calculated This Thesis	none
Ethylene Dichloride	I.C.T.	Tyrer L,M, & W	I.C.T.	Tyrer
Ethylene Dibromide	L,M, & W	none	Calculated This Thesis	none
Acetone	F,H, & A	none	Calculated This Thesis	none
n-Heptane	F,H, & A	none	Calculated This Thesis	none
Benzene	I.C.T.	Tyrer F,H, & A Rao	I.C.T.	Tyrer F,H, & A
Toluene	I.C.T.	F,H, & A	I.C.T.	F,H, & A
m-Xylene	I.C.T.		I.C.T.	
Fluorobenzene	L,M, & W	none	Calculated This Thesis	none

* B & R - Bhagavantam and Rao.
F,H, & A - Freyer, Hubbard, and Andrews.
L,M, & W - Lagemann, McMillan, and Woolf.
L,E, & M - Lagemann, Evans, and McMillan
I.C.T. - International Critical Tables.

TABLE V

CALCULATION OF THE ADIABATIC COMPRESSIBILITY
OF METHYLENE DICHLORIDE FROM SOUND VELOCITY

T °K	V_s M/sec	V cc/g	$K_S \times 10^6$ atm^{-1}
253.2	1250	0.715	46.37
273.2	1172	0.734	54.15
283.2	1132	0.744	58.83
293.2	1093	0.754	63.95*
303.2	1054	0.765	69.77
313.2	1015	0.776	76.32

Sample Calculation:

$$K_S \times 10^6 = \frac{V \times 10^6}{V_s^2}$$

At T = 293.2°K

$$K_S \times 10^6 = \frac{0.754 \times 10^6}{(1093 \times 10^2)^2} \text{ cm}^2/\text{dyne}.$$

Since 1 atm = 1.0133×10^6 dynes/cm^2

$$K_S \times 10^6 = \frac{0.754 \times 10^6 \times 1.0133 \times 10^6}{(1093 \times 10^2)^2} \text{ atm}^{-1}$$

$$= 63.95 \text{ atm}^{-1}.$$

*Lagemann, Evans, and McMillan have found $K_S \times 10^6 = 63.49$ as calculated from sound velocity.

It is not known whether the extrapolated compressibilities for n-heptane are reliable or not. Because of the size and complexity of the molecule and the considerable range over which the extrapolation is made, it is likely that the results near the melting point are not very accurate. Freyer, Hubbard, and Andrews[84] have shown that the sound velocity curve is not linear (though the deviation is not very large) near the melting point for benzene, aniline, bromoform, and α-bromonaphthaline. Rao[85] has also shown this for benzene.

It is estimated that for n-heptane an error of five per cent in the extrapolated K_S at the lower temperatures may occur. This error would cause the calculated C_v for these points to be in error from one to two calories.

Isothermal Compressibilities

For the calculations for C_v involving liquids for which the isothermal compressibilities have been calculated by Tyrer, or by Freyer, Hubbard, and Andrews, and/or reported in the International Critical Tables, the literature values were used. The results for carbon tetrachloride were recalculated for the reasons given in Chapter IV. The comparison is given in Table VI.

The accuracy of calculated isothermal compressibilities depends strongly upon the accuracy of the density and heat capacity data used.

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[84] E. B. Freyer, J. C. Hubbard, and D. H. Andrews, loc. cit.

[85] M. R. Rao, "The Adiabatic Compressibility of Liquids," J. Chem. Phys., loc. cit.

The importance of the density data is discussed by Tyrer.

TABLE VI

COMPARISON OF RESULTS FOR THE ISOTHERMAL COMPRESSIBILITY OF CARBON TETRACHLORIDE

T °K	Isothermal Compressibility x 10^6 atm^{-1}			
	Calculated This Thesis	I.C.T.*	Tyrer	F,H, & A*
273.2	89.3	91.2	91.03	89.7
283.2	96.6	98.3	98.31	97.0
293.2	104.8	106.4	105.96	104.8
303.2	113.3	114.5	114.34	113.3
313.2	122.7	123.6	123.94	123.2
323.2	133.1	133.8	134.97	134.4

*I.C.T. - International Critical Tables.
F,H, & A - Freyer, Hubbard, and Andrews.

The most probable source of error in isothermal compressibilities from the literature is heat capacity data used in their calculation. The workers whose results are used in this thesis have, however, evidently used very reliable data.

The literature search reported in Appendix I has shown that for many liquids the older measurements are as reliable as some of those made more recently. This is easily seen in the investigation of carbon disulfide (Figure 6) and chloroform (Figure 7) where the results of Regnault are in very good agreement with more recent measurements. Tyrer has used Regnault's heat capacities for calculating the isothermal compressibilities of these liquids. It is estimated that, at worst, heat capacities used by Tyrer, and Freyer, Hubbard, and Andrews

differ from values that may be read from the "best curves" of Appendix I by one per cent. The resultant difference in K_T is very small.

Density Data and Coefficient of Thermal Expansion

For the calculations of the isothermal compressibility, K_T, of carbon tetrachloride, ethylene dibromide, acetone, n-heptane, and fluorobenzene, the density data of the International Critical Tables[86] were used. The coefficient of thermal expansion, a, was calculated from this same density data. A sample calculation follows.

a. Sample Calculation: Coefficient of Thermal Expansion for Carbon Tetrachloride at 283.2°K

$$\frac{1}{V} = 1.63255 - 1.911 \times 10^{-3} t - 0.69 \times 10^{-6} t^2$$

$$-\frac{1}{V^2}\frac{dV}{dt} = -1.911 \times 10^{-3} - 1.38 \times 10^{-6} t$$

$$\frac{1}{V}\frac{dV}{dt} \times 10^3 = V\left[1.911 + 1.38 \times 10^{-3} t\right] = a \times 10^3$$

If $t = 10°C$, then

$$a \times 10^3 = \frac{1}{1.6134}(1.911 + 0.0138)$$

$$= 1.193\ °C^{-1}$$

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[86] International Critical Tables, op. cit., pp. 28-30.

Methylene Dichloride

The density data of Sugawara,[87] as presented in Dzung's paper,[88] were used in the calculations for methylene dichloride. Morgan and Lowry,[89] and Timmermans and Hennaut-Roland[90] have also measured the density of this liquid. The results of these investigators agree almost perfectly.

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[87] S. Sugawara, "Studies on the Thermodynamic Properties of Dichloromethane," J. Soc. of Mech. Eng. (Japan), 37: 491, 711, 1934.

[88] L. S. Dzung, loc. cit.

[89] S. O. Morgan and H. H. Lowry, "Dielectric Polarization of Some Pure Organic Compounds in the Dissolved, Liquid, and Solid States," J. Phys. Chem., 34: 2385 - 2432, 1930.

[90] M. J. Timmermans and Mme. Hennaut-Roland, "Travaux de Bureau International d'Etalons Physico-Chimiques. V. Etude des Constantes Physiques de Vingt Composes Organiques," J. de Chimie Physique, 29: 529-568, 1932.

APPENDIX III

INTERNAL CONTRIBUTIONS AND GAS HEAT CAPACITY DATA

This appendix presents the calculations of the internal contributions to heat capacity, C_i, used in the calculations of the extramolecular contributions, $C_v - C_i$, in Chapter III; or, if the calculation of C_i was not made in this thesis, states the source from which the value used was taken.

As stated in Chapter III, the internal contribution was assumed to be equal for liquids and gases at the same temperature; and, the calculations of this contribution for liquids were made from internal vibration frequencies of the molecule in the same manner as is usual in calculating the internal contribution to C_p^o for gases, or, C_i was calculated from C_p^o results found in the literature.

The calculations made of C_i in this thesis were made with the aid of the Planck-Einstein oscillator tables of Johnston, Savedoff, and Belzer.[91]

The choice of C_i for each liquid is discussed in the following paragraphs.

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[91] H. L. Johnston, L. Savedoff, and J. Belzer, Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom, Navexos P-646 (Washington: Office of Naval Research, Dept. of the Navy).

Carbon Tetrachloride and Chloroform

Vold[92] has calculated the vibrational contributions, C_i, and, therefrom, the ideal gas heat capacities, C_p^0, of several halomethanes, including carbon tetrachloride and chloroform. He compared his results with available experimental gas heat capacities, but found the latter somewhat discordant among themselves. His results for chloroform were, however, very near the mean of all the data for that gas. Pitzer[93] later made very precise measurements for carbon tetrachloride and concluded that the agreement between his results and Vold's calculations was very good.

In view of this agreement the vibrational heat capacities of Vold have been used for C_i in the calculation of $C_v - C_i$ for these liquids.

Carbon Disulfide

The vibrational contributions for carbon disulfide were calculated using the vibration frequencies of Dennison and Wright.[94] The calculations are given in Table VII. The gas heat capacities at 298.1 and 400 degrees were found thereby to be 10.89 and 11.84 cal/mole-°K, respectively, which may be compared with 10.91 and 11.85 as calculated

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[92]R. D. Vold, "The Heat Capacity of Methane and It's Halogen Derivatives from Spectroscopic Data," J. Am. Chem. Soc., loc. cit.

[93]K. S. Pitzer, "The Heat Capacity of Gaseous Hydrocarbons, Including Experimental Values for n-Pentane and 2,2-Dimethylbutane," J. Am. Chem. Soc., 63: 2413-2418, 1941.

[94]D. M. Dennison and N. Wright, "A New Long Wave-Length Absorption Band of CS_2," Phys. Rev., 38:2077, 1931.

TABLE VII

CALCULATION OF THE INTERNAL CONTRIBUTION FOR CARBON DISULFIDE*

$\tilde{\nu}$ cm^{-1}	w/T**	C^0 cal/mole-°K	w/T**	C^0 cal/mole-°K	w/T**	C^0 cal/mole-°K
	T 273.2°K		T 283.2°K		T 293.2°K	
655.5	2.399	0.800	2.315	0.848	2.236	0.895
396.8 (2)	1.452	2.797	1.401	2.864	1.353	2.926
1523	5.575	0.042	5.378	0.052	5.194	0.063
C_i(cal/mole-°K):		3.64		3.76		3.88
	T 298.1°K		T 303.2°K		T 313.2°K	
655.5	2.199	0.917	2.162	0.939	2.093	0.981
396.8 (2)	1.331	2.954	1.308	2.983	1.267	3.035
1523	5.109	0.069	5.023	0.076	4.863	0.090
C_i(cal/mole-°K):		3.94		4.00		4.11
	T 400°K					
655.5	1.639	1.275				
396.8 (2)	0.992	3.363				
1523	3.807	0.251				
C_i(cal/mole-°K):		4.89				

*C^0 - Contribution to Heat Capacity for One Vibrational Term: cal/mole-°K.
C_i - Internal Contribution to Heat Capacity: cal/mole-°K.
T - Absolute Temperature: degrees Kelvin.
$\tilde{\nu}$ - Wave Number: cm^{-1}.

**The tables of Johnston et al (loc. cit.) used in making these calculations have tabulated C^0 vs. w/T as well as the usual function, $x = 1.438w/T$. The former tabulation was used because it is obviously more convenient.

by Cross[95] from the same frequencies and the tables of Gordon and Barnes.[96] These results also agree almost exactly with those of Bhagavantam,[97] who made this calculation at 273.2, 293.2 and 313.2 degrees, using the same frequencies.

Brown and Manov[98] have determined the entropy by the third law method which they reported for the gas at 319.35 degrees as 57.48 eu versus the spectroscopic value of 57.60 eu calculated by them from the frequencies of Dennison and Wright. Cross has calculated the hypothetical ideal gas entropy at 298.1 degrees as 56.84 eu, and Kelley,[99] 56.86 ± 0.10 eu, which compares closely with Brown and Manov's third law value of 57.1 ± 0.4 eu at 298.16 °K.

Methylene Chloride

Glocker and Edgell[100] have shown that the fundamental frequencies used in previous gas heat capacity calculations on the methylene

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[95] P. C. Cross, "Thermodynamic Properties of Sulfur Compounds II. Sulfur Dioxide, Carbon Disulfide, and Carbonyl Sulfide," J. Chem. Phys., 3: 825-827, 1935.

[96] A. R. Gordon and C. Barnes, "Evaluation of the Series Which Arise in the Calculation of Thermodynamic Quantities from Spectroscopic Data," J. Chem. Phys., 1: 297-307, 1933.

[97] S. Bhagavantam, loc. cit.

[98] O. L. I. Brown and G. G. Manov, loc. cit.

[99] K. K. Kelley, Contributions to the Data on Theoretical Metallurgy. XI. Entropies of Inorganic Substances. Revision (1948) of Data and Methods of Calculation (Bumines Bul. 477. Washington: Dept. of the Interior).

[100] G. Glocker and W. F. Edgell, "Heat Capacity of Certain Halomethanes," Ind. and Eng. Chem., 34: 532-534, 1942.

halides were in error. They have presented the fundamental frequencies given by Wu[101] as being more satisfactory than any so far proposed. The vibrational contributions for methylene chloride have been calculated from the frequencies given in Glocker and Edgell's paper. The results are given in Table VIII.

Ethylene Dichloride

C_i was calculated by subtracting 4R from the C_p^o values of Gwinn and Pitzer.[102] These investigators have measured the gas heat capacity at moderately high temperatures and from a partition function including the potential barrier to internal rotation as determined from their measured values calculated the heat capacity at 250 and at 298.1°K.

Mizushima, Morino, Watanaba, Simanouti and Yamaguchi[103] have found that the ratio of trans to gauche isomers in the gas drops from 5:1 at 170°C to 2:1 at 150°C, while the ratio in the liquid at 25° is 1.8:1. This indicates that the potential barrier to internal rotation is considerably greater in the condensed phase. The effect of this on heat capacity at these temperatures is, however, small enough to be of no importance in the present calculations.

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[101] Wu Ta-You, Vibrational Spectra and Structure of Polyatomic Molecules (Shanghai: China Science Corp., 1939), pp. 243-250.

[102] W. D. Gwinn and K. S. Pitzer, loc. cit.

[103] S. Mizushima, Y. Morino, I. Watanaba, T. Simanouti, and S. Yamaguchi, "Raman Effect, Infra-Red Absorption, Dielectric Constant and Electron Diffraction in Relation to Internal Rotation," J. Chem. Phys., 17: 591, 1949.

TABLE VIII

CALCULATION OF THE INTERNAL CONTRIBUTION
FOR METHYLENE DICHLORIDE*

w cm^{-1}	w/T	C^0 cal/mole-°K	w/T	C^0 cal/mole-°K	w/T	C^0 cal/mole-°K
	T 253.2°K		T 273.2°K		T 283.2°K	
284	1.122	1.607	1.040	1.655	1.003	1.676
700	2.765	0.612	2.562	0.712	2.472	0.760
736	2.907	0.547	2.694	0.646	2.599	0.693
896	3.539	0.321	3.280	0.402	3.164	0.443
1149	4.538	0.124	4.206	0.172	4.057	0.199
1266	5.000	0.077	4.634	0.113	4.470	0.133
1425	5.628	0.040	5.216	0.062	5.032	0.075
2985	11.79	0.000	10.93	0.000	10.54	0.000
3046	12.03	0.000	11.15	0.000	10.75	0.000
C_i(cal/mole-°K):		3.33		3.76		3.98
	T 293.2°K		T 298.1°K		T 303.2°K	
284	0.969	1.694	0.953	1.703	0.937	1.712
700	2.387	0.807	2.348	0.829	2.309	0.852
736	2.510	0.740	2.469	0.762	2.427	0.785
896	3.056	0.485	3.006	0.504	2.955	0.527
1149	3.919	0.228	3.854	0.240	3.790	0.255
1266	4.318	0.154	4.247	0.165	4.175	0.177
1425	4.860	0.089	4.780	0.097	4.700	0.105
2985	10.18	0.000	10.01	0.000	9.845	0.000
3046	10.39	0.000	10.22	0.000	10.05	0.000
C_i(cal/mole-°K):		4.20		4.30		4.42
	T 313.2°K		T 323.2°K			
284	0.907	1.728	0.879	1.742		
700	2.235	0.895	2.166	0.937		
736	2.350	0.828	2.277	0.870		
896	2.861	0.567	2.772	0.608		
1149	3.669	0.285	3.555	0.316		
1266	4.042	0.202	3.917	0.226		
1425	4.550	0.123	4.409	0.141		
2985	9.531	0.000	9.236	0.001		
3046	9.725	0.000	9.425	0.000		
C_i(cal/mole-°K):		4.63		4.84		

* C^0 - Contribution to Heat Capacity for One Vibrational Term: cal/mole-°K.
C_i - Internal Contribution to Heat Capacity: cal/mole-°K.
T - Absolute Temperature: degrees Kelvin.
w - Wave Number: cm^{-1}.

Ethylene Dibromide

Gwinn and Pitzer[104] have also measured the gas heat capacity of ethylene dibromide, from 383 to 473°K, and assigned a potential barrier to internal rotation. They found it impossible, however, to get satisfactory agreement between the calculated curves and the experimental points for entropy, heat capacity, and dipole moment, with the same barrier, implying that either some frequencies were misassigned or the form of the potential function used was in error. This matter was discussed in Gwinn and Pitzer's paper.

C_i was calculated from the frequency assignments of Wu,[105] which were used by Gwinn and Pitzer, and the contribution of internal rotation from Gwinn and Pitzer's plot, reproduced here as Figure 11. This calculation is shown in Table IX. The C_p^0 values calculated from these internal contributions at the higher temperatures agree perfectly with those of Gwinn and Pitzer, as they should. The reason for our making the calculation at all is to obtain low temperature values for C_i. C_p^0 at low temperatures were not calculated in Gwinn and Pitzer's paper for ethylene dibromide as they were for ethylene dichloride, presumably because of the uncertainty in the form of the potential function for internal rotation, previously discussed. The error from this source, if any, is probably small enough to be unimportant for the present calculations. Additional restriction of

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[104] W. D. Gwinn and K. S. Pitzer, loc. cit.

[105] Wu Ta-You, loc. cit.

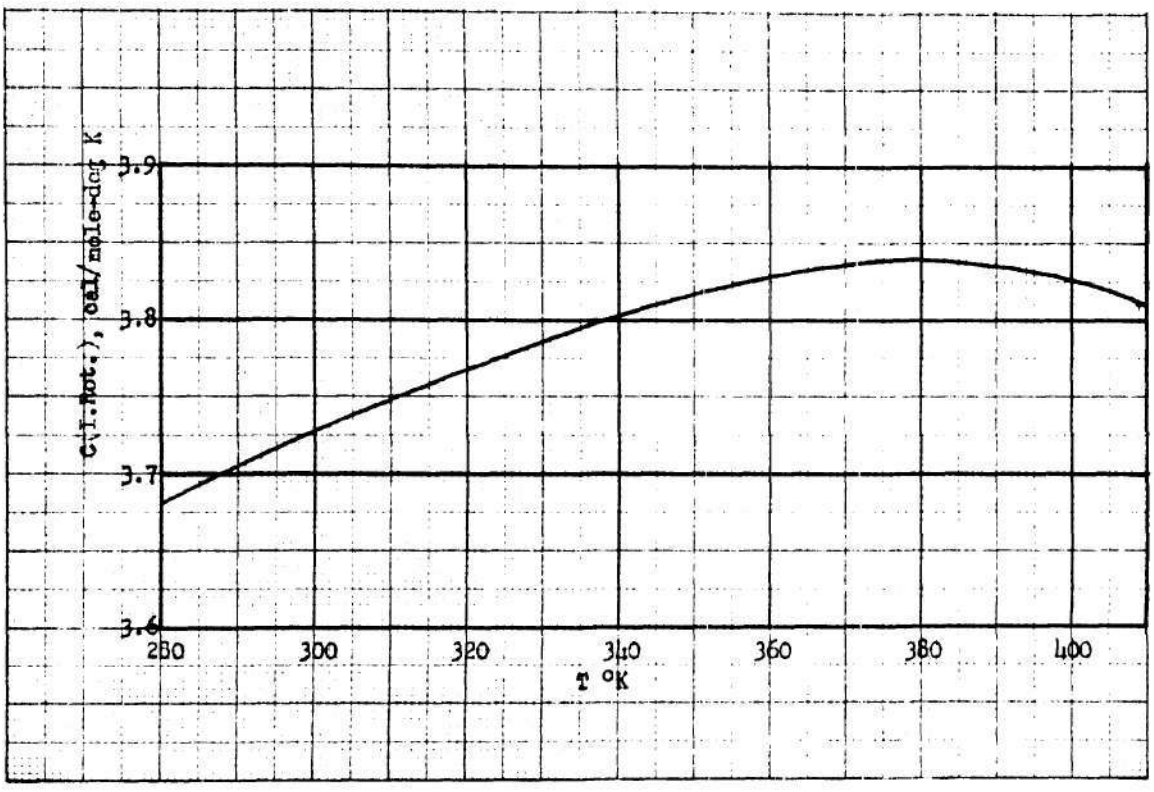

Figure 11. Gwinn and Pitzer's Plot of the Contribution of Internal Rotation to the Heat Capacity of Ethylene Dibromide

TABLE IX

CALCULATION OF THE INTERNAL CONTRIBUTION FOR ETHYLENE DIBROMIDE (1,2-DIBROMOETHANE)*

w cm^{-1}	w/T	C^0 cal/mole-°K	w/T	C^0 cal/mole-°K	w/T	C^0 cal/mole-°K
	T 283.2°K		T 303.2°K		T 323.2°K	
140	0.495	1.905	0.462	1.916	0.434	1.924
187	0.661	1.844	0.617	1.862	0.579	1.876
658 (2)	2.324	1.686	2.173	1.865	2.039	2.030
750	2.651	0.667	2.476	0.758	2.321	0.845
930	3.29	0.399	3.07	0.480	2.88	0.559
1063 (2)	3.76	0.525	3.52	0.652	3.29	0.797
1180 (2)	4.16	0.360	3.89	0.465	3.65	0.581
1418 (2)	5.00	0.155	4.67	0.217	4.38	0.290
1256	4.44	0.137	4.14	0.184	3.88	0.235
2995 (4)	10.6	0.000	9.9	0.001	9.28	0.002
C(I. Rot.):		3.690		3.735		3.775
C_i(cal/mole-°K):		11.37		12.13		12.92
	T 343.2°K		T 393.2°K		T 423.2°K	
140	0.408	1.931	0.356	1.944	0.331	1.950
187	0.545	1.888	0.476	1.911	0.442	1.922
658 (2)	1.920	2.182	1.672	2.507	1.556	2.660
750	2.188	0.923	1.907	1.099	1.774	1.186
930	2.70	0.643	2.361	0.822	2.200	0.916
1063 (2)	3.10	0.936	2.542	1.446	2.361	1.644
1180 (2)	3.44	0.700	3.00	1.016	2.79	1.201
1418 (2)	4.13	0.371	3.60	0.434	3.34	0.760
1256	3.66	0.288	3.19	0.607	2.97	0.522
2995 (4)	8.74	0.004	7.62	0.017	7.07	0.016
C(I. Rot.):		3.810		3.835		3.780
C_i(cal/mole-°K):		13.68		15.64		16.56

* C^0 - Contribution to Heat Capacity for One Vibrational Term: cal/mole-°K.
C_i - Internal Contribution to Heat Capacity: cal/mole-°K.
C(I. Rot.) - Contribution to Heat Capacity Due to Internal Rotation: cal/mole-°K.
T - Absolute Temperature: degrees Kelvin.
w - Wave Number: cm^{-1}.

internal rotation in the condensed phase also would have a negligible effect on the heat capacity, as discussed for ethylene dichloride.

Acetone

The internal contributions for acetone were calculated from the internal potential barrier and frequency assignments made by Schumann and Aston.[106] These calculations are given in Table K. They have calculated the entropy from these frequencies and obtained close agreement with the experimental entropy. The recent, careful analysis of the infra-red absorption spectra and fundamental vibrations of the acetone molecule made by Lecompte[107] suggest no frequency changes of sufficient magnitude to substantially affect heat capacity or entropy calculations.

C_p^o calculated from the C_i of this thesis were compared in Figure 12 with the calculated values of Dobratz[108] and the measurements of Bennewitz and Rossner[109] and of Collins, Coleman, and Devries.[110] The results of the latter were reported at one atmosphere and have been

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[106] S. C. Schumann and J. G. Aston, loc. cit.

[107] J. Lecompte, "Infra-Red Absorption Spectra and Modes of Vibration," J. Phys. Radium (8), 6: 127-133, 1945.

[108] C. J. Dobratz, "Heat Capacities of Organic Vapors," Ind. and Eng. Chem., 33: 759-762, 1941.

[109] K. Bennewitz and W. Rossner, "The Molal Heat of Organic Vapors," Z. Physik. Chem., B 39: 126-144, 1938.

[110] B. T. Collins, C. F. Colemann, and T. DeVries, "The Heat Capacities of Organic Vapors VI. Acetone," J. Am. Chem. Soc., 71: 2929-2930, 1949.

TABLE X

CALCULATION OF THE INTERNAL CONTRIBUTION FOR ACETONE

w cm^{-1}	w/T	C^0 cal/mole-°K	w/T	C^0 cal/mole-°K	w/T	C^0 cal/mole-°K
	T 273.2°K		T 300°K		T 330°K	
780	2.86	0.568	2.60	0.693	2.36	0.822
1070	3.66	0.288	3.57	0.312	3.21	0.657
1715	6.28	0.019	5.72	0.036	5.20	0.063
376	1.38	1.445	1.25	1.528	1.14	1.596
528 (2)	1.93	2.169	1.76	2.391	1.60	2.602
2950 (6)	10.8	0.001	9.83	0.002	8.94	0.005
1220 (2)	4.47	0.266	4.07	0.393	3.70	0.555
1432 (4)	5.25	0.238	4.77	0.393	4.34	0.604
950 (4)	3.48	1.352	3.17	1.766	2.88	2.236
C(I. Rot.)(2):		3.04		2.92		2.80
C_i(cal/mole-°K):		9.39		10.43		11.94
	T 350°K		T 400°K			
780	2.23	0.898	1.950	1.072		
1070	3.06	0.484	2.68	0.653		
1715	4.91	0.085	4.29	0.159		
376	1.074	1.635	0.940	1.710		
528 (2)	1.508	2.724	1.320	2.970		
2950 (6)	8.43	0.003	7.37	0.034		
1220 (2)	3.48	0.676	3.05	0.975		
1432 (4)	4.09	0.770	3.58	1.237		
950 (4)	2.71	2.542	2.37	3.267		
C(I. Rot.)(2):		2.78		2.62		
C_i(cal/mole-°K):		12.60		14.70		

* C^0 - Contribution to Heat Capacity for One Vibrational Term: cal/mole-°K.
C_i - Internal Contribution to Heat Capacity: cal/mole-°K.
C(I. Rot.) - Contribution to Heat Capacity Due to Internal Rotation: cal/mole-°K.
T - Absolute Temperature: degrees Kelvin.
w - Wave Number: cm^{-1}.

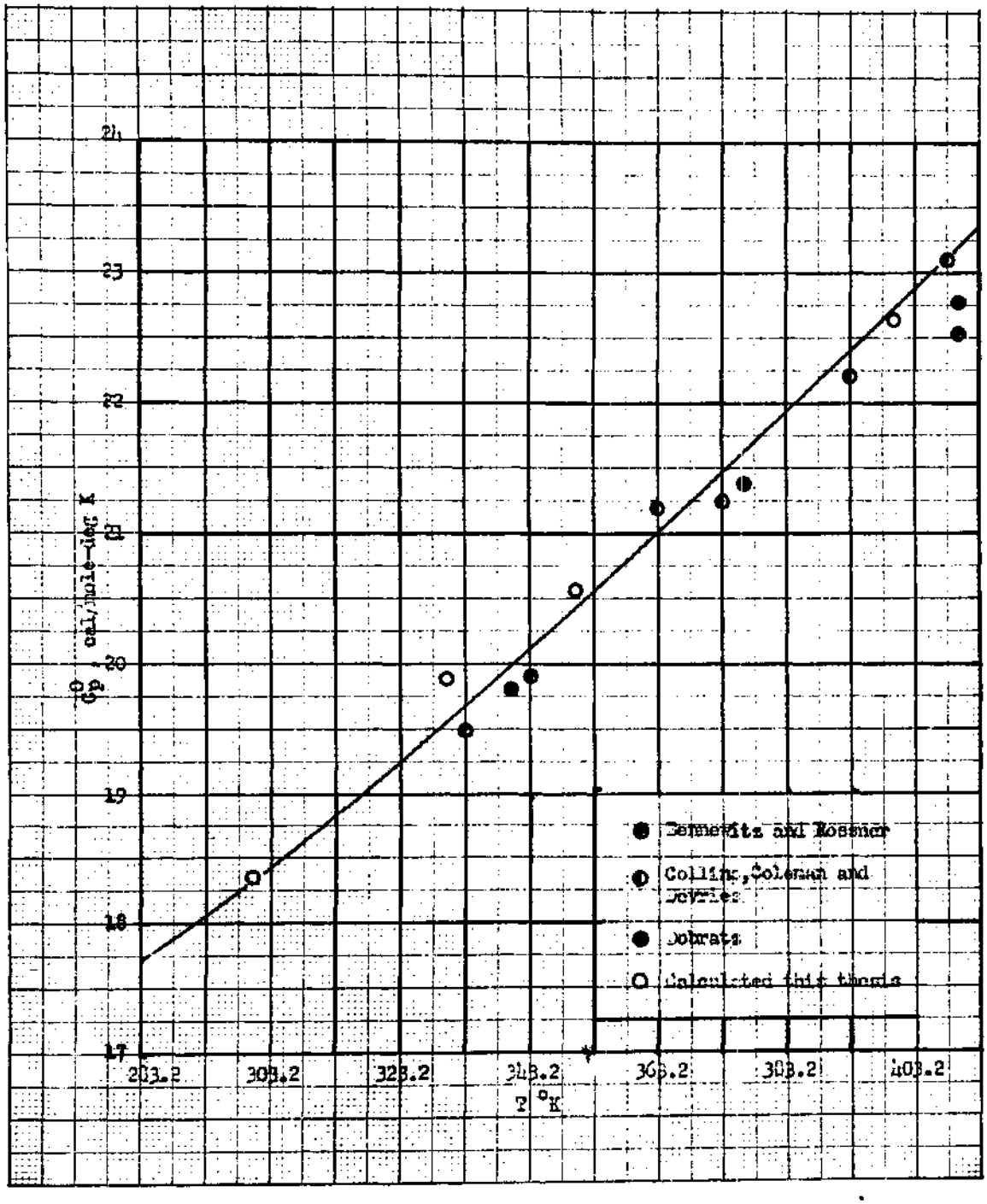

Figure 12. Heat Capacity of Gaseous Acetone

corrected to zero pressure for use in Figure 12 by the approximation of Watson and Smith[111] as reported by Dodge.[112]

n-Heptane

Pitzer[113,114] has measured the gas heat capacity of n-heptane at 423°K, assigned the potential barriers to internal rotation and the steric energy levels, and calculated C_p^0 down to 298.16°K. Measurements of Waddington, Todd, and Huffman[115] and values reported in the Selected Values of Properties of Hydrocarbons[116] are in nearly perfect agreement with Pitzer's results.

In order to obtain values at low temperatures, C_i was calculated in the present work by the method of Pitzer. The results of this calculation, using the notation of Pitzer,[117] are given in Table XI. The detailed calculations are not shown in this thesis. The calculation was made also at high temperatures in order to check the results.

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[111] K. M. Watson and R. L. Smith, Natural Petroleum News, July, 1936.

[112] B. F. Dodge, Chemical Engineering Thermodynamics (New York: McGraw-Hill Book Co., Inc., 1944), p. 243.

[113] K. S. Pitzer, "The Thermodynamics of n-Heptane and 2,2,4-Trimethylpentane, Including Heat Capacities, Heats of Fusion and Vaporization, and Entropies," J. Am. Chem. Soc., loc. cit.

[114] K. S. Pitzer, "Thermodynamics of Gaseous Paraffins, Specific Heat and Related Properties," Ind. and Eng. Chem., 36: 829-831, 1944.

[115] G. Waddington, S. S. Todd, and H. M. Huffman, "An Improved Flow Calorimeter. Experimental Vapor Heat Capacities and Heats of Vaporization of n-Heptane and 2,2,3-Trimethylbutane," J. Am. Chem. Soc., 69: 22-30, 1947.

[116] Selected Values of Properties of Hydrocarbons, Bureau of Standards C 461 (Washington: United States Government Printing Office, Nov., 1947), p. 284.

[117] K. S. Pitzer, "The Vibration Frequencies and Thermodynamic Functions of Long Chain Hydrocarbons," J. Chem. Phys., 8: 711-720, 1940.

TABLE XI

RESULTS OF THE CALCULATION OF THE INTERNAL CONTRIBUTION FOR n-HEPTANE*

T(°K):	183.2	203.2	223.2	243.2	263.2	283.2
$6C^0(C - C_{str.})$:	0.286	0.505	0.789	1.134	1.518	1.940
$5C^0(C - C_{bend.})$:	6.561	7.075	7.487	7.821	7.885	8.165
$4C^0$(I. Rot.):	8.72	8.88	8.96	9.08	9.20	9.28
$2C^0(CH_3)$:	3.970	4.351	4.778	5.297	5.772	6.295
$5C^0(CH_2)$:	0.425	0.765	1.241	1.844	2.579	3.427
C^0(steric):	1.947	1.888	1.828	1.729	1.630	1.550
C_i(cal/mole-°K):	21.91	23.46	25.08	26.90	28.59	30.66

T(°K):	303.2	323.2	343.2	363.2	400.0
$6C^0(C - C_{str.})$:	2.372	2.831	3.268	3.703	4.471
$5C^0(C - C_{bend.})$:	8.391	8.576	8.730	8.859	9.050
$4C^0$(I. Rot.):	9.30	9.31	9.30	9.25	9.16
$2C^0(CH_3)$:	6.802	7.324	7.891	8.395	9.420
$5C^0(CH_2)$:	4.363	5.390	6.472	7.590	9.733
C^0(steric):	1.391	1.252	1.192	1.079	0.999
C_i(cal/mole-°K):	32.62	34.68	36.85	38.88	42.83

Rotation of the end methyl groups is included in $C^0(CH_3)$.

* C^0 - Contribution to Heat Capacity for One Vibrational Term: cal/mole-°K.
C_i - Internal Contribution to Heat Capacity: cal/mole-°K.
C(I. Rot.) - Contribution to Heat Capacity Due to Internal Rotation: cal/mole-°K.
T - Absolute Temperature: degrees Kelvin.

Benzene, Toluene, and m-Xylene

The internal contributions for benzene, toluene, and m-xylene were calculated by subtracting 4R, R being the gas constant, from the C_p^o values reported in the Selected Values of Properties of Hydrocarbons.[118] These values are considered to be very reliable.

Fluorobenzene

The internal contributions for fluorobenzene were calculated from estimated C_p^o. Experimental C_p^o for fluorobenzene were available over a short temperature range, while C_p^o both calculated and experimental were available for benzene over a longer range. A "calculated" C_p^o curve for fluorobenzene was drawn by assuming that the calculated results for fluorobenzene would vary from the experimental results the same amount as in the case of benzene.

Within the range where experimental points were available for fluorobenzene, this is believed to be a good approximation; but, in order to obtain C_p^o at low temperatures the curve was extrapolated linearly over a considerable temperature range. It is not known whether or not the slope is correct at these lower temperatures.

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[118] Selected Values of Properties of Hydrocarbons, op. cit., p. 286.

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